VARTA

Sealed Nickel Cadmium Batteries

VDI-Verlag

Sealed Nickel Cadmium Batteries

Published by
Varta Batterie AG

1. FOREWORD

Sealed maintenance free nickel cadmium batteries have now become
very important items in instrumentation and other applications.

It seems to us that the time has now arrived to publish a comprehen-
sive account of this field of design and technical application. This
will make it easier for interested parties to learn the latest state of the
art because they will not have to search through the bulk of the litera-
ture published on the various aspects of the subject.

The staff of VARTA Batterie AG have pooled their knowledge and ex-
perience in the field of maintenance free sealed nickel cadmium bat-
teries to compile this book. In doing this, they have been able to draw
on the store of experience of a generation of their predecessors.
These were the pioneers, whose efforts laid the foundations for the
current technical achievements in sealed nickel cadmium batteries.

This book is dedicated as a source of information to all those who
come into contact with nickel cadmium batteries — scientists, deve-
lopment engineers, students and users. Our book should answer the
questions these people ask during the course of their work, helping to
solve the problems they find so interesting. Therefore, it contains not
only information on the scientific aspects of these cells, but includes
the field of actual manufacture and uses.

Co-authors:

Dipl.-Phys.	E. Buder
Dipl.-Ing.	F. W. Busemann
Dipl.-Ing.	B. Gnida
Dipl.-Ing.	H. Hocke
Dipl.-Ing.	H. A. Kiehne
Dr. rer. nat.	G. Knauel
	W. König
Dr.-Ing.	H. K. Köthe
Dipl.-Ing.	W. Raudszus
Dipl.-Ing.	W. Tietze
Dr. rer. nat.	J. Woidt

The compiling and overall supervision has been undertaken by Dipl.-Ing. W. Raudszus of the Technical Applications Department for sealed nickel cadmium batteries and Dipl.-Ing. H. A. Kiehne of the Central Applications Department.

English edition edited by F. R. Cloke, VARTA LIMITED.

To all the co-authors, and those who have not been named here, who have helped with this book and whose work has laid the foundations of present day practice, I hereby offer my gratitude.

Kelkheim, October, 1982

Prof. Dr. G. Lander

Director of VARTA Batterie AG and Head of VARTA Research and Development Centre in Kelkheim.

CHAPTERS

The rapidly developing state of battery technology results in a need to continuously update literature. In addition to this publication, VARTA publishes a wide range of leaflets which are related to specific cell types. Please contact VARTA in order to ensure that you possess the most up to date literature.

Due to our policy of continued development, details in this document may change without prior notice.

CONTENTS

2. Electrochemical Power Supplies

Electrochemical power supplies in the form of cells have been in use for so long that many users have forgotten how they work. This chapter presents a short and simple account of the basic principles that are common to all electrical couples.

Primary and rechargeable batteries are now available in a wide range of shapes and capacities. The world trade (excluding Eastern Block countries and military users) was more than US $ 7,500 million in 1976. This volume of trade proves how important electrical storage batteries have become. There are future developments waiting to be realised, e.g. higher energy densities, greater high rate discharge capacities, increases in maintenance free ranges and increased interchangeability.

Among the many methods of generating electrical power, first place is held by the dynamo — this is the source of power from the power stations which supply industry and homes. The second place is held by electrochemical cells, which can be divided into two major classes: primary cells and secondary cells.

Primary cells, mainly comprising those widely known as dry batteries, the most common being of the Leclanché type, because the electrochemical processes involved are non-reversible, cannot be recharged after they have delivered their stored energy.

Secondary cells are rechargeable because their electrochemical mechanisms are reversible. Some types can be charged and discharged hundreds or even thousands of times before they become unusable.

Both kinds of cells, primary and secondary, have the following fundamental properties:

— They are energy storage devices	(chemical energy)
— They are energy converters	(chemical energy → electrical energy)

A third group of electrochemical cells are known as fuel cells. They only perform the function of converting chemical energy to electrical energy, not that of energy storage. To give an example, in a fuel cell working at normal temperature the reacting gasses, hydrogen and oxygen, are supplied to the electrodes from pressure storage vessels in a continuous stream.

Understandably, there are also hybrid types such as those using atmospheric oxygen which could be described as half primary, half fuel cell.

Based on the series of elements that give rise to electrochemical voltages there is a large number of couples which can be used as energy stores, for example the immersion of two different metals or metal oxides in an aqueous electrolyte (Fig. 2/1).
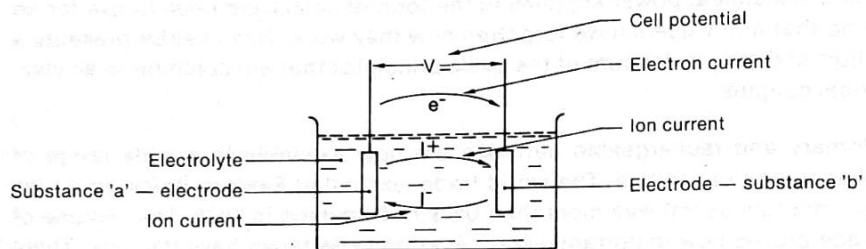
Fig. 2/1:
Components in an electrochemical cell

The substances used for electrodes 'a' and 'b' (e.g. metals or metal oxides) are chemically altered during the life of the cell, causing changes in the electronic charge of the materials and an electric current can be drawn from the cell. The total amount of energy available is determined by the amount of chemically alterable material in the electrodes.

With the exception of certain special types which operate decomposition reactions, for practical purposes all those couples are excluded which show unstable behaviour or whose potential is too low to be useful. In addition, other combinations which are too expensive to produce or which do not lend themselves to satisfactory production methods are also excluded. Next to the voltage generated, the usable energy or capacity in ampere-hours (Ah) is important, also the load currents and power-to-weight ratio; these can be specified per unit weight or unit volume. Reversibility is an obvious criterion with rechargeable or secondary cells.

Figs. 2/2 and 2/3 show the practical values attained for specific energy per unit volume and unit weight respectively. It can be seen that the sealed nickel cadmium batteries considered in this book do not compare favourably in these respects, however, their trouble-free operation and their ability to be recharged a large number of times is a considerable advantage to their end user.

Besides the fundamental voltage and capacity properties, there are another series of factors important in certain operating conditions, for example, temperature behaviour, mechanical strength. These factors are considered in detail in later chapters.
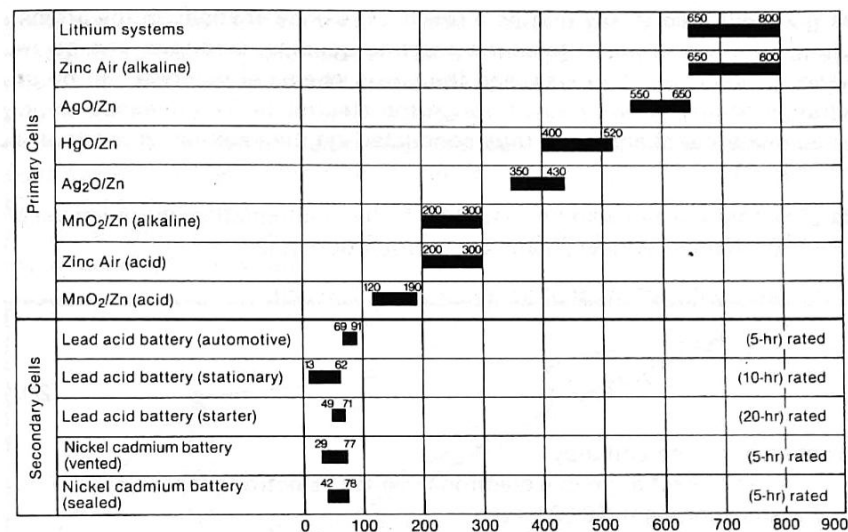
Fig. 2/2:
Energy density of primary and secondary batteries (in terms of Wh/l)
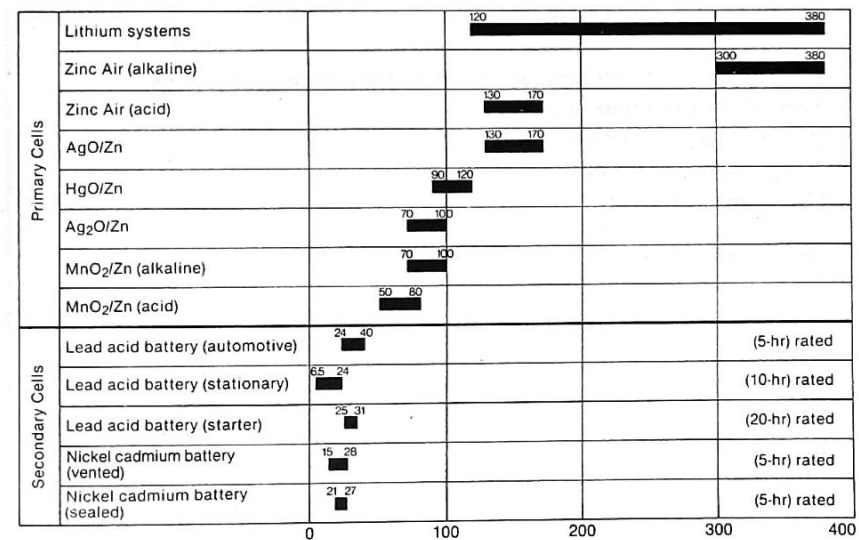
Fig. 2/3:
Energy density of primary and secondary batteries (in terms of Wh/kg)

The processes which take place within an electrochemical cell during discharge or charge can be described in several different ways.

It is generally true to say that as a result of valence changes in the atoms, molecules, or ions which form the reacting couples, electrons can be released or absorbed. This happens through a chemical reaction, i.e. by an exchange of ions which travel through the electrolyte. The released or absorbed electrical charges are thus conducted via the external circuit to and from the cell.

This phenomenon can also be described by the mathematical formulae used by Prof. Dr. August Winsel (1) and Dr. Dietrich Berndt (2).

For the reversible potential of an electrochemical cell:

$$V_o = -\frac{\Delta G}{z \cdot F} \qquad [2/1]$$

ΔG change of free enthalpy
z   number of exchangeable electrons in either electrode reaction
F   Faraday constant (96 500 As)

and for the concentration-dependant standard E.M.F. equation derived from it by Nernst:

$$V_o = V_{o.s} - \frac{RT}{zF} = \Sigma \cdot v_i \ln a_i \qquad [2/2]$$

$V_{o.s}$ Equilibrium cell potential at activity 1 for all the substances
a_i Activities of the reacting couples
v_i Stoichiometric ratios
T   Absolute temperature
R   Molar gas constant

For the capacity of an electrochemical storage cell:

$$C = \int_{t=o}^{t=t_E} I(t)\, dt \qquad [2/3]$$

C   Capacity
I   Discharge current
t   Discharge period
t_E Time to reach end-of-discharge voltage

It is obvious that there will be side reactions, which are caused by necessary or by unwanted impurities, but these are disregarded here. Details of these are given in the following chapter which describes sealed nickel cadmium batteries. There are theoretically many possibilities of making electrochemical cells by combinations of the different elements. Most of these combina-

tions are excluded for practical purposes because only after a number of associated problems have been solved will they perform as useful power supplies. The "Babylonian Tower" shown in Fig. 2/4 includes a number of theoretically possible galvanic couples. These and many others have been studied in the VARTA Research and Development Centre in Kelkheim, but to the present day only a few systems are technically practical, economical, producible, and hence generally useful. Examples of these are lead acid, nickel iron, nickel cadmium batteries, manganese oxide, silver oxide, mercury oxide, and more recently lithium cells.
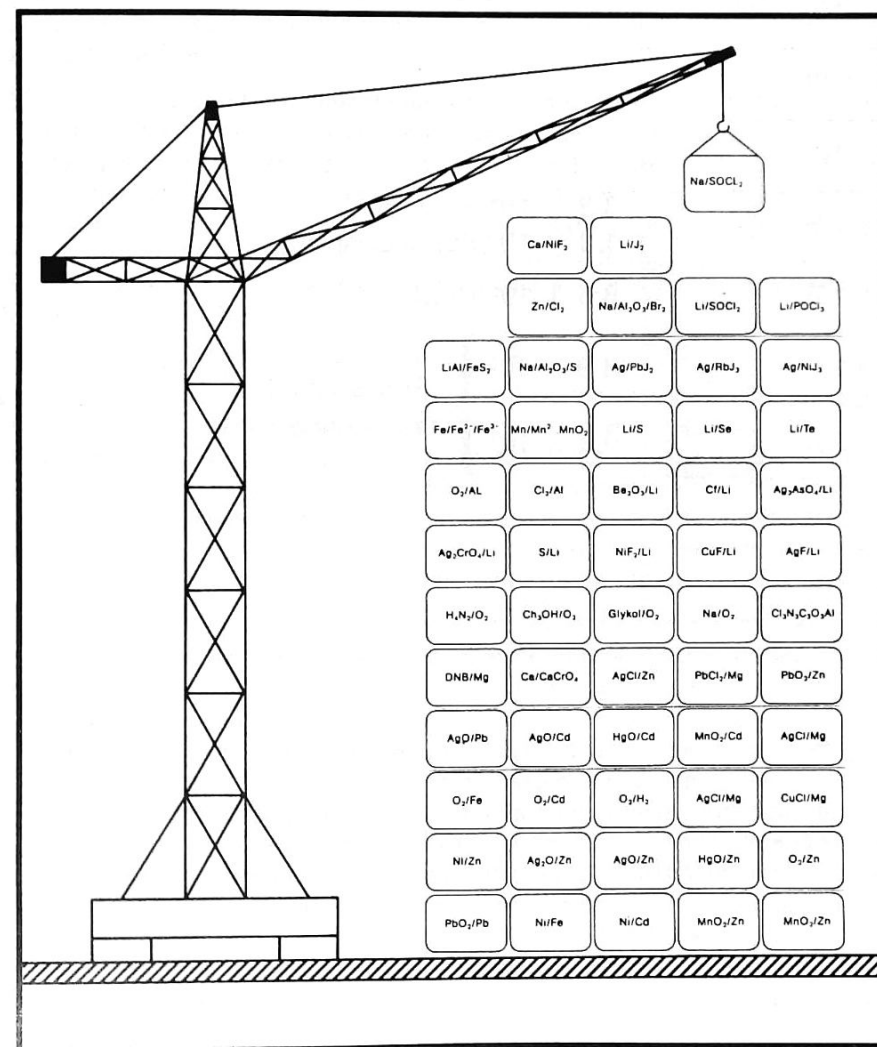
Fig. 2/4: "Babylonian Tower" of electrochemical couples

Wh/kg

10^{10}		$1,2 \times 10^{10}$ Fast breeder reactors
10^9		
10^8		$1,7 \times 10^8$ Uranium-235
10^7		
10^6		
10^5		
10^4		$3,3 \times 10^4$ Hydrogen $1,3 \times 10^4$ Petrol/Gasoline
10^3		$8,5 \times 10^3$ Coal
10^2		$3,8 \times 10^2$ ⎫
10^1		$0,2 \times 10^1$ ⎬ Primary and Secondary Cells
10^0		
0		
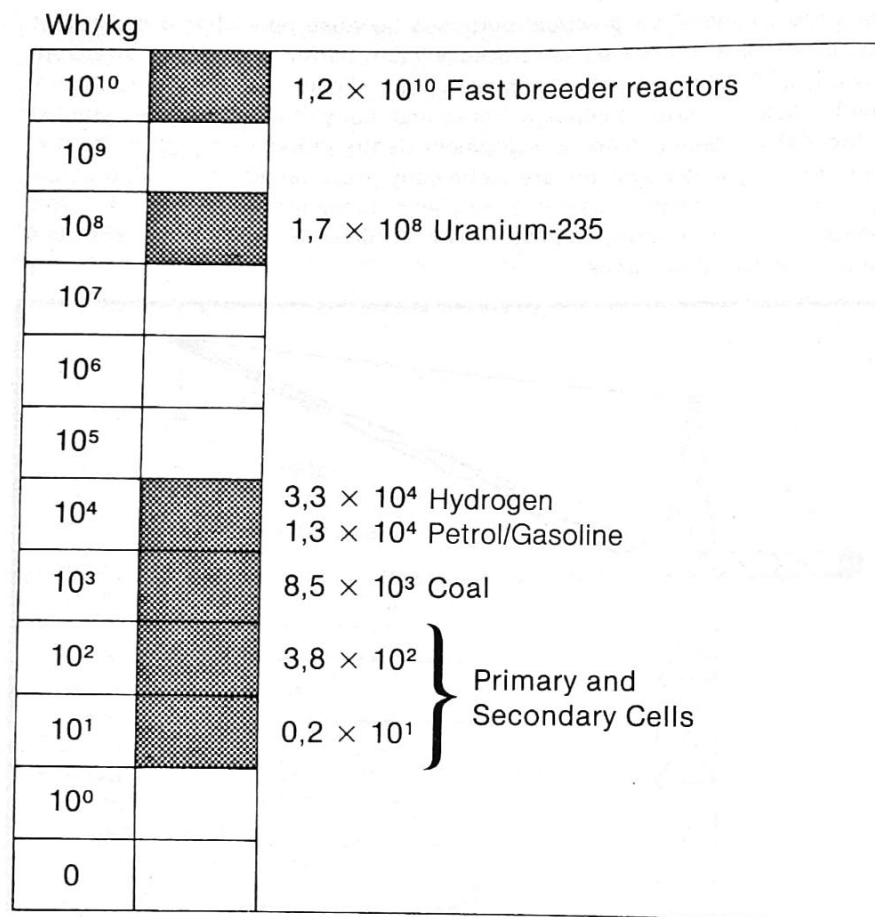
Fig. 2/5: *Energy densities of various energy carriers and sources*

Fig. 2/5 shows the position of electrochemical cells in the field of various types of energy sources and carriers. It clearly shows the limitations of so-called "portable power", into which category sealed nickel cadmium batteries belong. The fact that these batteries in their sealed form occupy such an outstanding position among the various electrochemical cells is due, largely, to their truly maintenance free operation. This is a basic requirement for "portable power" and makes them particularly suitable for industrial and technical use. Many other battery systems require attention in the form of topping up, and this has to be done by automatic devices or recombination methods before they can be described as maintenance free.

3. History of the sealed nickel cadmium battery

Mankind has always dreamed about increasing his muscular power by portable aids. The invention of the battery made this dream a reality and today we take this assistance for granted. It has been a long and hard struggle to make portable power supplies in the forms now available but that path has been followed by VARTA.

The initial ideas and experiments are attributed to Alessandro Volta, who in 1799 built the voltaic pile named after him and thus made the first practical portable electric power supply — a primary cell. In 1802 Johann Wilhelm Ritter discovered that he could recharge his "Ritter pile", and the secondary cell was born, henceforth known as the accumulator or storage battery. Gaston Planté in 1859 constructed the first truly useful form of the rechargeable battery, a lead storage battery with sulphuric acid electrolyte of a definite density.

About 1890, and in the subsequent years, Thomas Alva Edison in America, and simultaneously Waldemar Jungner in Sweden developed the alkaline battery with potassium hydroxide as the electrolyte. Both used nickel hydroxide for the positive electrode, but Edison in America (1901) used iron for the negative electrode and Jungner used cadmium. Some years later the alkaline principle was extended by Yardney in America, who devised the silver-zinc cell for special purposes. This had a particularly good power-to-weight ratio, but at the expense of very high cost and low cyclic ability, i.e. useful life.

In the course of his development work in the field of steel cased nickel iron batteries Edison had by 1912 succeeded in developing a sealed battery which would work under certain conditions. He filed a patent, based on the recombination of hydrogen and oxygen, which is evolved during charge into the cell's spare space. These gasses are evolved in all rechargeable cells. A heated platinum wire ancillary electrode assisted the recombination of these gasses forming water. However, this cell worked for several reasons not fully satisfactory and was not used commercially mainly because of the high cost of the platinum it was not economical, and the fact that it could not be used in any working position.

It is a fundamental requirement of all sealed batteries that they be completely sealed, that they can be charged and discharged in any position, and that they do not require the maintenance needed by open batteries, particularly topping up with water. The need to avoid this disadvantage is as old as the alkaline battery itself. Mere hermetic sealing of the case does not solve the

problem because the evolution of gasses during overcharge would soon lead to swelling and eventual bursting of the case.

The first significant step in the direction of a sealed nickel cadmium battery arose from the developments of Adolf Dassler, A. Erich Lange, Erich Langguth, and Edmond Breuning (3) to whom a basic patent was granted in 1933. These four inventors, among whom Dassler and Langguth were colleagues at VARTA (at that time AFA), had discovered that with sufficient area, oxygen could be electrochemically reduced on metal plates, i.e. on the charged cadmium electrode of a nickel cadmium battery. By achieving optimum electrode dimensions, it was found possible to recombine oxygen and to prevent the evolution of hydrogen. But not until Georg Neumann's development work between 1947 and 1951 was a commercial cell possible, and his practical solutions to the manufacturing problems were soon followed by others (4).

From about 1950 onwards, VARTA brought on to the market the first sealed batteries made by mass production methods. VARTA was an amalgamation of the well known companies AFA (Akkumulatoren-Fabrik Aktiengesellschaft), DEAC (Deutsche Edison Akkumulatoren Companie), and the former Pertrix GmbH, in whose laboratories the principle of the sealed battery had been discovered. These batteries could be safely overcharged but could not be safely overdischarged. This disadvantage was overcome through the development by Dassler of "antipolar mass", included in the positive electrode. This invention was patented by Dassler in 1951.

The pioneering achievements of the VARTA Organization in the field of sealed nickel cadmium batteries are indisputable and have resulted in several hundred patents awarded to VARTA in Germany and abroad. The granting of licences to leading companies in the most important industrial countries such as U.S.A. and Japan show the outstanding importance of the VARTA Company in this growth area of battery production. The many millions of sealed nickel cadmium batteries which have been sold since the start of commercial production in 1950 are proof of this; in a great variety of forms they are well known throughout the entire world.

1950 saw the start of mass production of sealed rechargeable nickel cadmium batteries in the form of button and cylindrical cells with mass plate electrodes. Rectangular cells appeared in 1951, also with mass plate electrodes. The breakthrough into large scale production came in 1954 with the manufacture of button cells for use in rechargeable pocket torches, and more than 200 million of these cells have now been sold.

New applications have led to a continued development of this system. The demand for ever increasing energy densities and high rate discharge led, in 1956, to the development of the first pressed electrode for use in a cylindrical cell made in the size of a single dry cell (R 20). By 1956 also a button cell had been produced for wristwatches, having one electrode which also served for

the back of the watch and was made of gold or stainless steel. In 1958/1959 came an important improvement to the then current button cell, a range of high rate discharge cells, the DKZ series. In parallel with this development, the first sealed nickel cadmium cell with sintered electrodes, rectangular in form, it was available for sale in 1958. At the end of 1958 there followed the first sealed cylindrical sintered electrode cells (round cells), which following continuous development, have been available since 1976 in the form of very high rate discharge sintered cells (RSH Model).

Today, VARTA's production in the field of sealed nickel cadmium batteries embraces button cells with capacities between 10mAh and 1Ah, cylindrical sintered cells with capacities between 100mAh and 7Ah and rectangular sintered cells with capacities between 2.4Ah and 50Ah. These have been used in a very wide range of applications, some of which are mentioned below, e.g. rechargeable pocket torches, hearing aids, electric pocket calculators and watches, electronic photoflash, emergency lights, burglar alarms, telephones, medical apparatus, measuring instruments of many kinds, as well as radio transmitters and receivers for the control and motive power of model aircraft, boats and cars, computer memory support.

The rapid development of this trouble-free, reliable, and economical power supply in the field of electronics will certainly lead to an even wider range of applications.

4. Design and Construction of Sealed Nickel Cadmium Batteries

4.1 Introduction

Of all the known alkaline couples, the electrode reactions in the nickel cadmium cell are certainly the best known today, and have been investigated most intensively. The reason for this is not only that this type of cell has been in commercial production for decades, and has such interesting reactions in the electrodes that scientists are probing ever more deeply into the mechanisms involved, but also that the system possesses such a multitude of applications.

As in all galvanic cells, the nickel cadmium cell consists of:

— positive and negative energy storing electrodes,
— the electrolyte,
— the separator, an insulator between the electrodes,
— and the cell or battery case.

The basic construction is the same for all the types manufactured; electrodes, separator, and type of electrolyte are often the same in both sealed and open batteries.

4.2 Cell Construction

4.2.1 Electrode Types

The electrodes form the core of every battery. They contain the electrochemically active materials or mass, and by their size and construction effectively determine the capacity at normal or peak load, charging characteristic, self discharge, useful life, internal resistance, and all other electrical properties. All electrodes contain as their major component, the active mass, such as nickel hydroxide for the positive electrode and cadmium hydroxide for the negative electrode. In order to improve the poor electrical conductivity of these materials, conducting agents are added to them; powdered nickel or graphite are the preferred additives. To improve the current flow, the active mass forming the electrodes is generally enclosed by a good metallic conductor.

Examples:
Pocket Plate Electrodes
A mechanically very reliable and robust type of electrode is now made with nickel hydroxide for the positive plate and cadmium hydroxide for the negative, with powdered nickel or graphite added and the mixture pressed into

nickel plated perforated steel pockets (Fig. 4/1). These so-called pocket plate electrodes, which are predominantly used in vented alkaline batteries, achieve a useful life of more than 10 years, due to their rugged external structure. This type's high weight is a disadvantage, 50% of the total electrode weight is in the form of this external covering. As a result, the specific capacity for the positive electrode amounts to approximately 65Ah/kg, and about 90Ah/kg for the negative.

Fig. 4/1:
Pocket Plate Electrode
Width of Strip Pockets 12 mm
Electrode Dimensions Depend on
Cell Type

Button Cell (Mass Plate) Electrodes

In other types of electrode, for example those used in sealed button cells (Chapter 7), the external covering takes the form of a thin nickel mesh. To improve the mechanical strength, the mixed materials are pressed, together with the conductive additive, into tablets and thus formed into a thin electrode which remains intact when subjected to evenly distributed pressure (Fig. 4/2). The mass plate electrode covering of nickel mesh has the primary duty of conducting electrons into and out of the active mass during charge and discharge respectively; it can only add slightly to its mechanical strength. As a result, this type of electrode achieves a capacity/weight ratio of about 100Ah/kg. As the pressed tablet requires evenly distributed support in order to maintain its structural integrity, e.g. a cell case which conforms to the shape of the electrode, small sealed button cells having capacities of up

to 1Ah utilize this type of electrode. The pocket plate electrodes are predominantly used in vented storage batteries with capacities up to 1,250Ah.
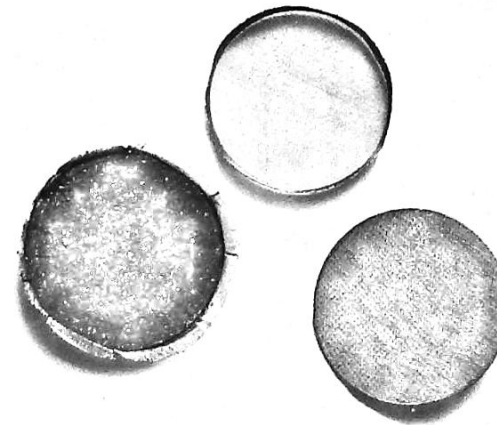
Fig. 4/2:
Mass Plate Button Cell electrode
Above — nickel wire mesh cup.
Below left — cup with mass 'tablet' inserted.
Below right — Completed electrode, a nickel gauze cover completing the enclosure

Sintered Foil Electrodes

For good electrical properties, particularly at high discharge rates and for satisfactory utilization of the active mass in galvanic cells, the crucial factors are the thickness of the layer of active material and the degree of electrode surface cover. Thin electrodes are necessary in batteries that are required to have high nominal charge and discharge rates, which are to work at low temperatures, and there must be a high proportion of conductive material to carry the current. These demands have been satisfied by the use of the sintered nickel plate electrodes, known since the 1930's, and now incorporated in both open and sealed cells. Their low inherent resistivity is their major advantage.

Sintered plate electrodes vary in thickness from 0.5 mm to 1 mm. They consist of a grid, generally made of perforated nickel plated sheet steel, on which nickel powder has been spread and sintered at about 1,000 °C under controlled conditions to inhibit chemical changes. This forms a highly porous, flexible layer with a porosity of about 80% (Fig. 4/3). The electrochemically active mass is impregnated into the pores of this sintered grid by a sequence of processes, starting with a salt solution, e.g. nickel or cadmium nitrate. The grid is dipped in this solution, so that the pores (diameter 15 µm or 0.015 mm) can absorb the liquid. After that, the sintered grid is dried and in the subsequent precipitation process, the nickel or cadmium salt is converted into the

electrochemically active mass, consisting of nickel hydroxide and cadmium hydroxide respectively. The precipitation can be simply expressed by the equation for the nickel hydroxide electrode as an example:

$$Ni(NO_3)_2 + 2KOH \rightarrow Ni(OH)_2 + 2KNO_3 \qquad [4/1]$$
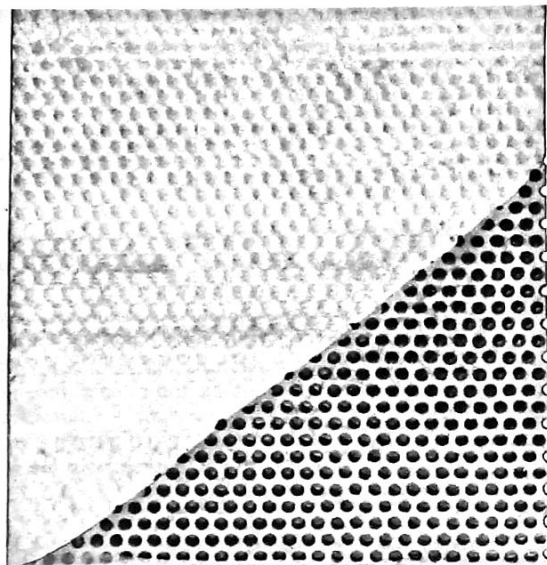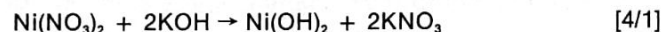
Fig. 4/3:
Sintered grid electrode. The lower part of the picture shows the perforated plate with the sintered mass removed. Hole diameter is 2 mm
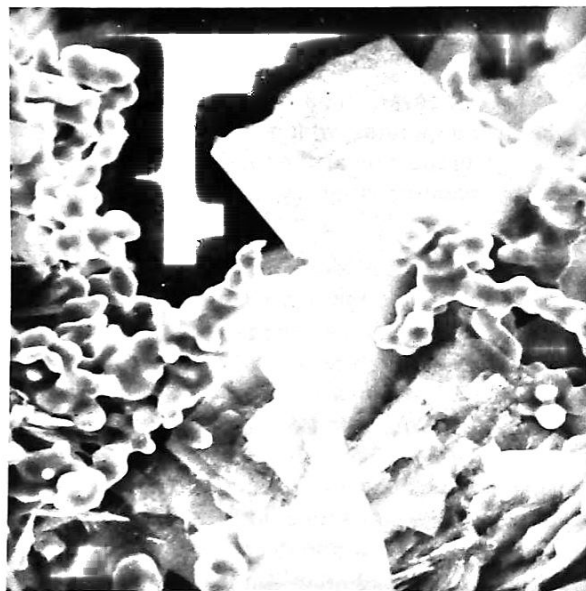
Fig. 4/4:
Negative sintered electrode seen under scanning electron microscope at 2,400 x magnification

The products of this reaction, potassium nitrate and nitrate ions must be removed from the grids by a very careful and thorough washing process because their presence would lead to a unacceptably high self discharge rate (section 5.6.2).

Due to different densities of nickel nitrate and nickel hydroxide the process steps:

— saturation with salt solution
— drying
— precipitation
— washing
— drying

must be repeated several times until the grids contain a pre-determined amount of nickel hydroxide. The amount of the electrochemically active mass determines the capacity and other electrical and mechanical properties (section 4.3.1.1) of the sintered electrode and hence that of the battery.

The cadmium hydroxide electrode is prepared in a similar way to the nickel hydroxide electrode. Fig. 4/4 shows a pore enlarged 2,400 times under a scanning electron microscope (S.E.M.). The large crystals with smooth surfaces are electrochemically active cadmium hydroxide, the small rounded ones are part of the conductive sintered nickel grid. The nickel sinter carrier grid is not only responsible for conducting current efficiently but has to provide a stable mechanical carrier to prevent shedding of the active mass, particularly under over-discharge conditions. The performance of these electrodes during impact and vibration tests is significantly better than that of the otherwise very rugged pocket plate electrodes.

The main advantages of the sintered electrode are its thinness, the very large area of accessible active material, in addition to the outside surface area, brought about by the high degree of porosity, and the efficient bonding of the active material to the carrier grid. Material utilization and the ability to deliver and receive high currents are therefore excellent. Even though the grid and the supporting framework make up about 50% of the total electrode weight, the specific capacity amounts to 120Ah/kg of electrode and therefore is more than the corresponding figure for mass plate electrodes.

4.2.2 Separators
Separators, like the electrodes, are a vital part of the galvanic cell. Their importance extends beyond their major duty of separating the electrodes of both polarities from each other. The type of separator has an effect on

— the useful life of the cell, particularly at high temperatures
— voltage characteristic at discharge rates
— charging conditions

— current supplied at low temperatures
— self-discharge
— reliability of the cell under vibration and impact

The separator directly or indirectly affects almost all the characteristics of the cell and hence, its suitability for various operational requirements. A good separator for sealed nickel cadmium batteries must satisfy the following criteria:

1. Reliable separation of positive and negative electrodes.
2. Effective prevention of movement of particles between electrodes of opposite polarity.
3. High electrical resistance (insulation), simultaneous with —
4. minimum resistance to the ionic flow within the electrolyte.
5. Mechanical and chemical stability over a wide temperature range (—50 °C to 70 °C)
6. Ability to absorb and retain electrolyte.
7. Permeability to gasses.
8. Flexibility.

Although separators have been continually improved, not all the above requirements can be satisfied optimally and simultaneously with the materials at present available. Therefore, a number of different materials are used for specific types of construction and application (5).

Fig. 4/5:
Separator mesh
magnified 100 times

Polyamide and polypropylene fibres are most often used today for the separators in sealed nickel cadmium batteries; made up into a web or mat, and woven. Fig. 4/5 shows such a polyamide fibre mat at 100 x magnification. The fibres lie randomly and at various distances apart. At the places with close fibre spacing the electrolyte is particularly well retained by capillary forces. A continuous chain of such places brings about electrolyte contact between the electrodes. At the same time a number of less tightly meshed places are necessary to allow gas bubbles to pass freely between the electrodes in sealed batteries (see items 6 and 7 of the criteria stated above). However, there must also be high absorption and retention of electrolyte because these two features have an important effect on the cell capacity and ability to supply high currents. In order that sealed cells can successfully withstand overcharging (section 4.4.3), they contain a precise amount of electrolyte so that the pores of the electrodes are saturated and those of the separator are only partly filled with electrolyte. With this amount of electrolyte, none can escape when the battery is operated in any position. Performance is not, therefore, affected by cell orientation.

Items 1, 2 and 5 of the criteria stated above are determined by the porosity and the pore structure, i.e. the pore size and distribution within the separator. Whereas high porosity is preferred for the flow of ions between the electrodes, the individual pores must be small enough to retain particles of the active material down to colloidal orders of magnitude. Furthermore, the porosity and pore distribution must not vary on a macroscopic scale because gross inequalities lead to uneven current density distribution over the active mass of the electrodes. The consequence of that would be uneven use of the active material and possibly early failure of the cell.

The chemical stability of the separator is crucial for long useful life of the cell, it must resist the electrolyte or oxidation by the oxygen which is generated during charging and which in sealed cells forces its way through the separator (section 4.4.2).

Especially strict criteria apply to the separator in the nickel cadmium system. The decomposition of a polyamide mesh in potassium hydroxide, aided by oxygen evolved at one electrode, is about 8—10 times as fast as for a mesh which for the same period is immersed in electrolyte only. In addition to oxygen, temperature has a critical effect on separator decomposition and helps the oxidation which can lead to the destruction of the separator. A temperature rise in the electrolyte from 20 °C to 40 °C brings about a fourfold increase in the rate of oxidation.

With the exception of chemical stability, polyamide fibre as a material meets all the requirements of sealed cells. This material is so quickly oxidized at high temperatures that on these grounds alone the operating temperature must be limited to 45 °C. Occasional excursions to excessive temperature

are less injurious than continuous operation at the maximum operating temperature. Oxidation of the separator implies that the separator fibres are dissolved, so that taken to the limit there is no longer any insulating material between the electrodes. The oxidation products themselves contribute to an increase in the carbonate content and nitrogen compounds in the electrolyte and hence adversely affect the capacity and the charge retention of the battery.

Polypropylene separators have proved to have a very high resistance to oxidation and, therefore, are chosen for cells that have to operate in high ambient temperatures (e.g. 60 °C). However, the high resistance to oxidation brings a disadvantage in that the absorption and retention of the potassium hydroxide solution is not as good as with polyamide materials. The consequences of this are impaired performance for sealed cells at high discharge rates, at room temperature and even more significantly at low temperatures. The low absorption of electrolyte can be explained by the very smooth surface and difficulty in forming a mesh with this synthetic fibre. Research work by the fibre manufacturers has confirmed this point. Comparison of these two fibres, polyamide and polypropylene, when used in sealed nickel cadmium batteries shows that both have individual advantages and disadvantages. Individual peculiarities are experienced in different application areas so that one material cannot be substituted for the other without causing changes in the performance of the batteries.

4.2.3 Electrolyte
Besides the electrodes and the separator the electrolyte is another vital part of a galvanic cell and hence of the nickel cadmium battery. The function of the electrolyte is to participate in electrochemical reactions with the positive and negative electrodes during charge and discharge. Normally the electrolyte shows distinct changes in its specific gravity when performing its function (e.g. the well known changes in its specific gravity of the acid in lead batteries). It is a peculiarity of the nickel cadmium cell that the changes in electrolyte density during the reactions at the positive and negative electrodes are equal and opposite and almost cancel each other out. The electrolyte in nickel cadmium cells is, therefore, ostensibly not a participant in the charge and discharge reactions. Diluted potassium hydroxide is generally used for the electrolyte in nickel cadmium cells. Its main advantages lie in its good conductivity, and low freezing point (2).

4.2.3.1 Electrolyte Conductivity
The conductivity of the electrolyte is an important factor in battery performance, for at high discharge rates the internal voltage drop is one of the

phenomena controlled in part by the conductivity of the electrolyte. Fig. 4/6 shows the specific conductivity of various alkaline electrolytes (6). The maximum conductivity of 0.42 (S/cm) for sodium hydroxide (NaOH) and 0.63 (S/cm) for potassium hydroxide (KOH), at a specific gravity of d = 1.26 kg/l (freezing point: — 46 °C).
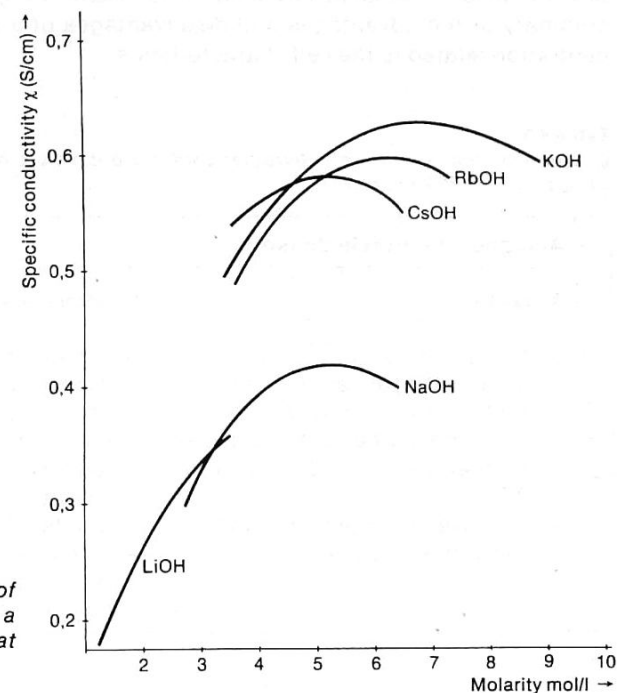
Fig. 4/6:
Specific conductivity of alkaline electrolytes as a function of molarity at 25 °C

This figure shows that cells with potassium hydroxide electrolyte perform much better at high discharge currents than those with sodium hydroxide; hence potassium hydroxide is used almost exclusively for nickel cadmium cells.

4.2.3.2 Electrolyte Specific Gravity
Research has proved that the stored capacity of a battery may be increased by approximately 10% if the specific gravity of the electrolyte is selected at a value higher than that at its maximum conductivity, i.e. about 1.27 kg/l (= 6.5 mol/l) (Fig. 4/6) but at about 1.30 kg/l or as Gossenberger (7) has stated 1.35 kg/l (8.6 mol/l). This fact can be explained when the electrode reactions which take place during charge and discharge are considered (section 4.3.3). The obvious advantage achieved by the gain in capacity is at the expense of the

useful life, particularly that of the sintered electrode; the various separator materials will oxidize faster and thus the service life of the cell is reduced. The specific gravity values at present used in nickel cadmium cells are a compromise and depending on the type of cell structure (chapter 7) lie between 1.24 and 1.30 kg/l. Potassium hydroxide at a specific gravity of 1.34 kg/l is only used in isolated circumstances. Table 4/1 gives a comprehensive summary of the advantages and disadvantages of a higher electrolyte concentration related to the cell characteristics.

Table 4/1:
Qualitative summary of cell characteristics for potassium hydroxide specific gravity values 1.27—1.35 kg/l at 20 °C

At higher electrolyte density	
Advantages	Disadvantages
— higher useful capacity (Ah) and energy (Wh) at various loads — higher Ah — and Wh — improvement when discharged at temperatures (—20 °C to + 45 °C) — improved charged retention — lower freezing point	— higher internal cell pressure during overcharge as the result of reduced oxygen solubility in the electrolyte — reduced service life for sintered electrode cells because of greater electrode swelling — increased oxidation of separator material (particularly polyamide)

(Properties)

4.2.3.3 Temperature Effects
Temperature affects the conductivity and viscosity of the electrolyte, and hence the cell characteristic.

Fig. 4/7 shows the critical relationship between the conductivity and viscosity of potassium hydroxide as a function of temperature. With a reduction in temperature, the conductivity of the electrolyte falls, causing a rise in the internal resistance of the cell and a higher internal voltage drop during discharge.

The figure also shows how the viscosity falls sharply as the temperature rises, so that at low temperatures the diffusion velocity of the electrolyte ions is greatly reduced; this leads to higher internal resistance, which so far as the user is concerned exhibits itself as greater voltage drop during discharge and higher on-charge voltage (section 5.1.2). The problems of operation at low temperatures are increased when the application requires high charge and discharge currents.

These physical principles lead to the conclusion that high electrolyte concentrations are desirable where batteries are intended for operation at high rates of discharge or at low temperatures. (See table 4/1 in section 4.2.3.2.)

Fig 4/7:
Conductivity χ (———) and viscosity (----) of potassium hydroxide (6.9 mol/l) as a function of temperature
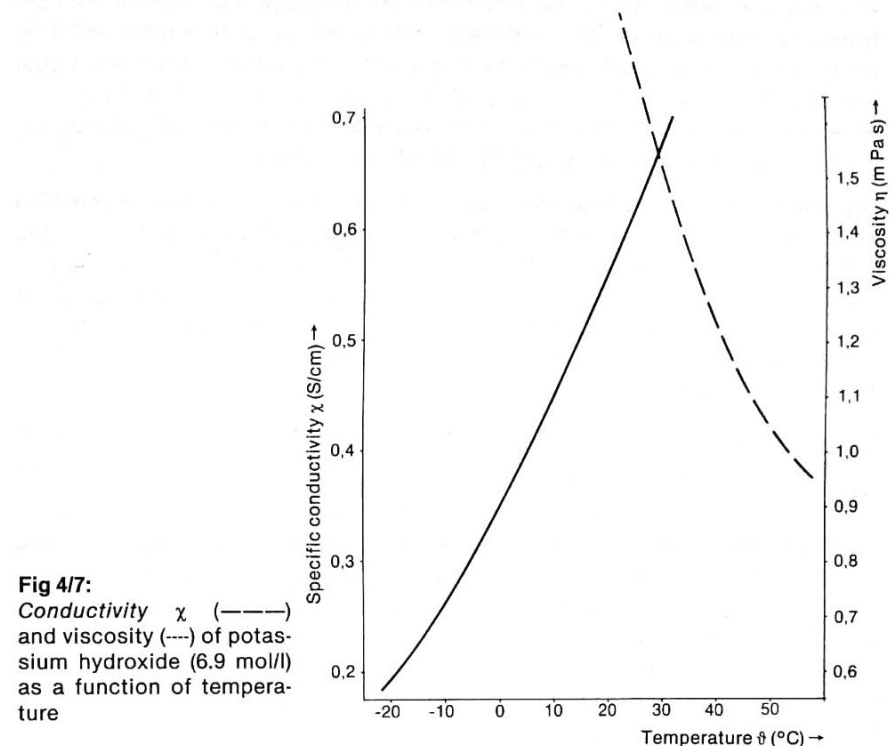
4.3 Electrode and Cell Mechanisms
Similar types of electrode are often used in both open and sealed nickel cadmium cells (section 4.2.1). The chemical reactions are similar when charging and discharging, and so is the calculated heat of reaction. The amount of heat produced is related to the type of plates used, the cell size and it varies greatly when comparing open and sealed cells. The thermodynamic reactions of open nickel cadmium cells will be discussed and then the related reactions within sealed cells will be considered.

4.3.1 The Nickel Hydroxide Electrode

4.3.1.1 Raw Materials and End Products During Charge and Discharge

The charge and discharge reactions at the positive electrode of a nickel cadmium cell are very complex because the reaction products depend on the methods of manufacture and the previous history of the electrode material. For example, nickel hydroxide which has been precipitated from a concentrated solution of nickel nitrate differs crystographically from nickel hydroxide which has been produced by cathodic deposition from nitrate solutions. The hydroxides so obtained have been designated as β-nickel hydroxide respectively α-hydroxide by Prof. Hans Bode and co-workers (8), and by Dr. Welf Dennstedt, Dr. Werner Löser (9) and other scientists.

The important point is that the material is an aqueous divalent hydroxide which varies in the type, amount, and the bonding of water in the crystal. Both water content and the manner of its bonding have a significant effect on the oxidizability of nickel-(II)-hydroxide. Anhydrous β-nickel hydroxide is not able to be easily fully oxidized, therefore, the active mass which is contained in the electrode consists of aqueous nickel hydroxide with a portion of structurally bonded water.

In β-nickel hydroxide this water is located in lattice defects in the crystals (up to $0.1\ H_2O/Ni(OH)_2$) and consequently the oxidation processes can penetrate the material.

Quite different from this is the hydroxide with a high water content which is designated as α-nickel hydroxide and which is shown in schematic form in Fig. 4/8. The crystalline structure of this material can be described as a hexagonal layer lattice; however, the individual nickel hydroxide layers are separated from each other by an intermediate layer, which in the ideal case is occupied by water molecules. In practice however, depending on the conditions during the production process, other molecules or ions, e.g. nitrate ions can be incorporated in this layer (section 4.2.1).
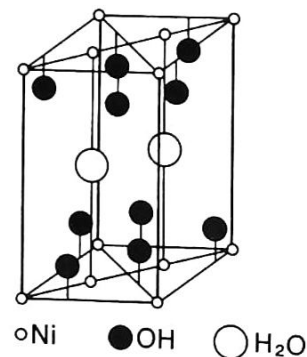
Fig. 4/8:
Schematic lattice structure of α-nickel hydroxide $3Ni(OH)_2 \cdot 2H_2O$

○Ni ●OH ○H_2O

Research has shown that the increased water content in α-nickel hydroxide (up to $0.55\ H_2O/Ni(OH)_2$) is very firmly bonded into the structure (9). This water content is of great importance for the oxidizability of the nickel hydroxide as active electrode material. During the fluctuations between charge and discharge of the electrodes the electrochemical processes in the active mass occur to an increasing extent via the α-phase, with a change in the composition, so that the β-phase originally produced during the manufacture of the electrode is converted.

The α-nickel hydroxide has in consequence of its higher water content a greater volume compared with β-nickel hydroxide and, therefore, needs more space in the grid, thus:
The volume of the crystal unit cells of α- and β-nickel hydroxide are in the ratio of 1.6 to 1.

During the first cycles of a cell's life, and especially during overcharge, there is a partial conversion of β-phase nickel hydroxide to the oxidized α-phase, which has also been designated as γ-phase by Bode and his co-workers (10). This change causes the mass to swell and can lead to considerable mechanical stress within the body of the electrode, so that under unfavourable circumstances it can become damaged.

Charge and discharge of the nickel hydroxide electrode are electrochemical processes by which the active mass of the electrode is oxidized and reduced in turn. The oxidation is not accompanied by absorption of oxygen but by emission of hydrogen. This hydrogen, in the form of protons, is removed from water molecules and hydroxide groups by charge equalization.

During charge (oxidation) electrons (e⁻) are drawn out of the nickel atoms via the cell terminals away from the electrode, and at the same time protons (H⁺) from the active mass diffuse through the electrolyte. For each nickel hydroxide phase, both of which can occur simultaneously at the positive electrode, this process can be described by the theoretical reaction equations below concerning charge and discharge of the α- and β-nickel hydroxide phases:

β-(II)-nickel hydroxide $\rightleftharpoons$ β-(III)-nickel hydroxide

$$Ni(OH)_2 + 2\ H_2O - H^+ - e^- \xrightarrow[\text{discharge}]{\text{charge}} Ni(OH)_2(OH) \rightarrow NiOOH + H_2O \qquad [4/2]$$

$$[6\ Ni(OH)_2]\cdot(4\ H_2O) + 2\ KOH - 10\ H^+ - 10\ e^- \xrightarrow[\text{discharge}]{\text{charge}} [4\ NiO_2 \cdot 2\ NiOOH]\cdot(2\ KOH, 2\ H_2O) + 2\ H_2O \qquad [4/3]$$

Principal Interlayer   Principal   Interlayer
Layer   Layer

α-(II)-nickel hydroxide $\xrightarrow[\text{discharge}]{\text{charge}}$ γ-nickel hydroxide
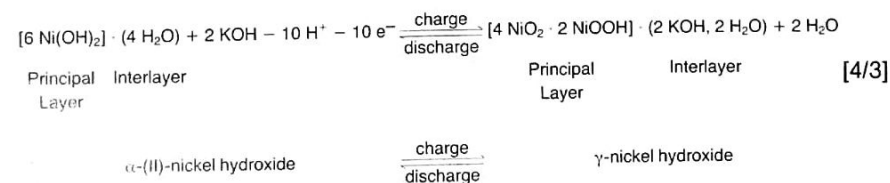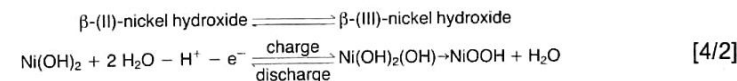
The formulae given in the reaction equations set limiting values too for the composition of the chemical compounds. In practice, these are considered in context with prevalent practical considerations and anyway become altered in a variety of ways via differing operational conditions. More often, mixtures between charge and discharge products occur, or, other factors being excluded, the chemical composition of the phase concerned can vary between certain limits. The oxidized nickel hydroxides are not stoichiometric compounds. As already mentioned (section 4.2.3), the KOH balance during charge and discharge reactions is virtually unchanged. This is obvious for the β-reaction; it also holds under practical circumstances for the α-γ-reactions. Within the cell, there remains the KOH incorporated in the γ-phase, also after discharge (reduction) contained in the active mass, because on reduction the pure α-phase will no longer be reached but only a partly oxidized α-nickel hydroxide, whose KOH content is approximately that of the γ-phase.

The utilization of the nickel hydroxide during charge and discharge can be described as a difference of degree of nickel oxidation between the charged and discharged active mass:

In the discharged material of the β- and α-phases the degree of oxidation in both cases theoretically equates to +2, which is equivalent to the symbol $NiO_{1.0}$. In the charged (oxidized) material of the pure β-phase it reaches the value of +3 ($NiO_{1.5}$), which can be found from the formulae [4/2] and [4/3]. For the oxidized α-phase material, which is also designated as γ-phase the value is theoretically +3.67 ($NiO_{1.83}$). The difference in degree of oxidation therefore lies at 1 for the β-β-reaction, and 1.67 for the α-γ-reaction. This comparison shows the importance of the utilization of the α-γ-reaction (Fig. 4/9), because the difference of 1 in the degree of oxidation signifies a storage capacity of 28.9 Ah per 100 g nickel hydroxide.
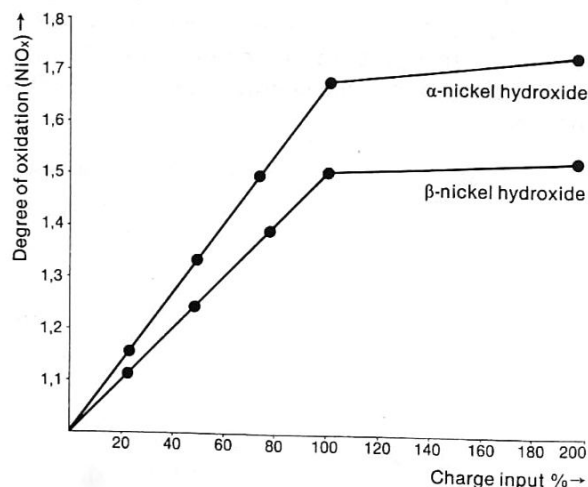
Fig. 4/9:
Degree of oxidation at potentiostatic oxidation of α- and β-nickel hydroxide as a function of charge input

This figure shows the analytically determined oxidation values for β- and β-nickel hydroxide as a function of the amount of current stored (given in % of the current stored up to the start of oxygen being evolved) (10). The degree of oxidation rises linearly as the energy is stored, as far as the 100% limit (start of oxygen evolution), and on further charging the degree of oxidation rise is insignificant. For total oxidation as found in practice, the break point for α-nickel hydroxide is at $NiO_{1.75}$ and for β-nickel hydroxide at $NiO_{1.5}$.

Discharge proceeds in the reverse direction, but in practice the initial condition (degree of oxidation +2) is not quite reached. This inherent disadvantage in the utilization of the material is however balanced out by the improved charge acceptance and charge availability, which is of greater importance in practice.

4.3.1.2 E.m.f., Capacity
The important electrode potentials during charge and discharge, which are stated in equations [4/2] and [4/3] for the α-phase were determined by Bode and his co-workers (8) against a reference electrode. Fig. 4/10 shows the degree of oxidation as a function of voltage. It is worth noting that not only oxidation but also reduction proceeds over a very small voltage range, which for oxidation is about $\Delta V \approx 30mV$. Reduction however does not take place over the same range but at about 100mV less relative to oxidation. Consequently the potential of the positive electrode is dependent on the current direction, i.e. whether the electrode is charged or discharged. Even at greatly reduced current densities during charge and discharge, for which the electrical resistance and the concentration effects of the electrolyte are small, the large potential difference between charge and discharge remains the same.
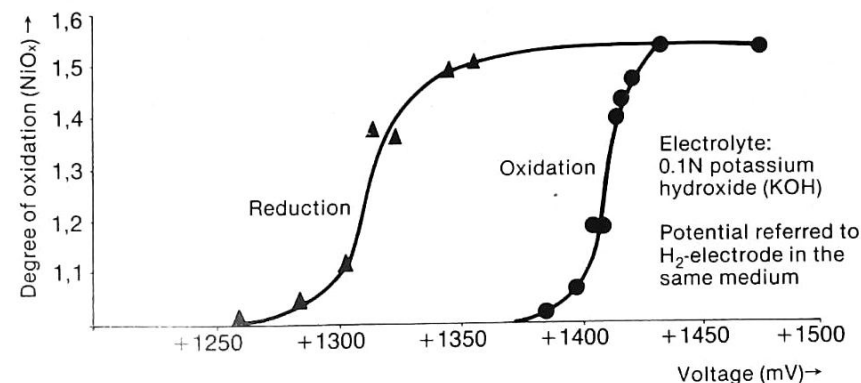
Fig. 4/10:
Degree of oxidation of β-nickel hydroxide as a function of voltage

From the thermodynamic viewpoint this signifies that the reactions do not have a characteristic of a reversible electrochemical system, as is possible with the negative cadmium/cadmium hydroxide electrode (section 4.3.2.2), or with the lead dioxide/lead sulphate electrode in the lead-acid cell.

The potential of the electrode reaction is dependent on the electrolyte concentration following the equation given by Nernst (see also Chapter 2, equation [2/2]).

By considering the statements made in section 4.3.1.1 about the potential of the reaction

$$\beta\text{-Ni(OH)}_2 + OH^- \rightleftarrows \beta\text{-NiOOH} + H_2O + e^- \qquad [4/4]$$
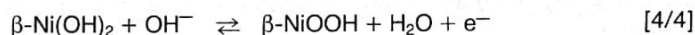
D. Berndt (2) has reported the value $V_0 = +0.490$ Volt in an electrolyte of OH^- ion activity $a_{OH^-} = 1$.

Assuming that the valence of nickel changes close to one, e.g. varies from the divalent $Ni(OH)_2$ to the trivalent $NiOOH$ — or in other words from $NiO_{1.0}$ to $NiO_{1.5}$ — and without taking into account the constitutional water, a capacity value of $289mAh/g$ $Ni(OH)_2$ can be calculated. This value of capacity is the theoretical limit for nickel hydroxide, whereas in practice the capacities actually attained are $265mAh$ for sintered electrodes and $160mAh/g$ $Ni(OH)_2$ for button cell electrodes. When the active mass is mixed with a conductor and if the weight of the electrode grid is taken into account (section 4.2.1) then the following capacities are obtained:

positive pocket plate electrode: ca. 65mAh/g electrode
positive button cell electrode: ca. 100mAh/g electrode
positive sintered electrode (thickness: 0.63 mm)   ca. 126mAh/g electrode

The electrode capacities are also affected by:
1. The production process of the nickel hydroxide.
2. Type and distribution of the conductive additive relative to the active mass (section 4.2.1).
3. Electrode reinforcement.

The capacities stated refer to small discharge currents. For higher discharge currents, the specific capacities of thin sintered electrodes, which contain large amounts of conductive nickel additive, are significantly better when compared with other types of electrode.

4.3.1.3 Effect of Foreign Ions on the Nickel Hydroxide Electrode
As stated in section 4.3.1.1, the structure of the nickel hydroxide and the oxidation products formed during charge are dependent on manufacturing methods and operating conditions. With changes in the type of construction, the physical and electrochemical properties of the nickel hydroxide will also vary.

The changes of the phases within the cell are not always desirable because the conversion of the β-nickel hydroxide in the vigorously swelling γ- and α-phases can lead to the state when the strength of the electrode grid is no longer able to resist destruction by swelling.

There are several possible ways of limiting this effect:
1. By limiting the charge/discharge conditions so that high currents in particular are avoided.
2. Reinforcing the electrode to strengthen it so that it can sustain the swelling (the disadvantage is a reduced energy density).
3. In sintered electrodes the amount of active mass can be so regulated that a sufficiently high pore volume is obtained for the swelling to be accommodated.
4. By adding other types of hydroxide which have a stabilizing effect on the β-phase and which inhibit the transition into the actively swelling γ- and α-phases.

Research work has been performed several times on the effect of foreign ions on the nickel-hydroxide electrode (11, 12).

In this connection, it has not only been shown whether the anti-swelling additives work, but also how they affect the electrochemical behaviour of the electrodes during charge and discharge. Pertinent factors here are:
— charge acceptance (efficiency) at different currents,
— capacity during discharging,
— temperature effects on the capacity,
— charge retention,
— voltage characteristic during charge and discharge.

If there is the intention to obtain a strengthening of the structure or some effect on the electrochemical behaviour of the nickel hydroxide by adding cations, then the important elements worth considering are only those with an ionic radius only slightly different from that of Ni^{2+}.

These elements can form mixed crystals with the nickel; the foreign ions substitute for the nickel ions in the major structural layers in the crystal lattice. Examples include cadmium (Cd) and cobalt (Co). Notwithstanding the statement about ionic radius above, it is also possible to consider elements which are significantly smaller than the nickel ion for they can occupy lattice defects in the crystal. Thus lithium (Li) can be incorporated by adding it to the electrolyte via which it reaches the nickel hydroxide electrode and is bonded into the crystal lattice.

Besides the binary mixed hydroxides, (nickel-metal)-hydroxides, Peter Ness (13) has prepared ternary mixed hydroxides of cadmium, cobalt, magnesium, and manganese with nickel, and tested them in the form of pressed powder electrodes. His paper includes research details and a discussion of results. The most important additives used today in sealed nickel-cadmium batteries are cadmium, cobalt and lithium. Their effects on the electrochemical and physical behaviour of the nickel hydroxide electrode are discussed below.

Cadmium (Cd)

Cadmium is regularly used in positive sintered and button cell electrodes. Depending on the production processes and amount added, the cadmium has an electrochemical effect and takes part in the cell reactions during charge, discharge, and reversal of polarity, or affects the nickel hydroxide structure just by its presence. If it is electrochemically active it forms cadmium hydroxide in the charged and discharged positive electrode, or metallic cadmium during polarity reversal, the reactions concerned are the same as those occurring in the negative electrode in the cell during charge and discharge (section 4.3.2).

For button cell electrodes, cadmium oxide is added to the positive electrode. For sintered cells, the electrode is treated with a cadmium salt, e.g. cadmium nitrate, and this becomes electrochemically active. On the other hand, if 10% by weight or less of cadmium nitrate is added to the nickel nitrate impregnating solution used during the manufacture of positive sintered electrodes (section 4.2.1) then this amount of cadmium can be homogeneously incorporated into the β-nickel hydroxide on precipitation (14). The cadmium-nickel hydroxide so formed only has a marked effect as a swelling inhibitor, and does not participate in the electrochemical reactions. The effective swelling control in the electrode during overcharge is proportional to the cadmium content in the nickel hydroxide lattice. No detrimental effects have been observed when cadmium has been added.

Cobalt (Co)

Similarly cobalt forms a mixed hydroxide with nickel when it is precipitated as a hydroxide from a solution of one of its salts simultaneously with the nickel. The electrochemical properties are advantageous in some respects but there can be detrimental effects. The most satisfactory effects are obtained with a 20 mol% cobalt addition according to S. Lerner (Table 4/2), (15).

The charge efficiency of sintered electrode cells is improved when charged at low rates and in high ambient temperatures because of a change in the oxygen overvoltage (section 5.2.6). A change in the kinetics of the electrode reaction during charge under these conditions brings about a retardation in parasitic oxygen evolution. Consequently more current is utilized for storing energy instead of evolving oxygen, i.e. the charging efficiency and the cell capacity are improved.

The inherent disadvantage of depressed discharge voltage caused by the addition of cobalt means that a compromise must be sought, while remembering that the amount added is critically affected by the intended operating conditions (section 5.5). For sintered nickel cadmium cells that are intended for high discharge currents it is recommended that cobalt additive should not be used. However, it is advantageous to add cobalt to cells designed for discharging at the 1-hour rate as a maximum, even if they are for use at high ambient temperatures. The improvement in capacity compared with electrodes without cobalt can be as much as 30%.

With mass plate electrodes (e.g. those used in button cells, or the pocket plate type), nickel-cadmium-cobalt hydroxide (composition 90:5:5 wt. %) has a beneficial effect on the resistance to swelling and the capacity of the cell (16). Not only does the treatment reduce the electrode swelling during charge and discharge, but the specific capacity of the nickel hydroxide is improved by about 15%.

Table 4/2:
Effect of cobalt addition on the electrochemical behaviour of nickel hydroxide electrodes

Favourable Effects	Unfavourable Effects
1. Improved charge efficiency (section 5.2.6) during charge of sintered cells at low rates (e.g. $0.3 \cdot I_{10}$) and at high ambient temperatures (e.g. 45 °C). The effect increases with the cobalt content. 2. Better charge retention at high ambient temperatures. 3. Reduction in swelling, and increase in capacity for mass plate electrodes containing ternary (Ni,Co,Cd)-hydroxide.	1. Decrease in the average discharge voltage of about 20 mV to 70 mV. The effect increases with the cobalt content. 2. Reduced capacity during high rate discharge.

Lithium (Li)

The addition of lithium to nickel-cadmium cells causes very different effects depending on cell type and its operating conditions, because in addition to a number of advantages, some unavoidable disadvantages will also arise. Lithium is more often added to vented cells than to sealed cells. The addition is always made by way of adding lithium hydroxide (LiOH) to the electrolyte, from which a fraction of the lithium ions (Li^+) are taken up by the positive nickel hydroxide electrode. Because of the smaller ionic radius of 60 pm

($\triangleq$ 0.6 Å) (by comparison Cd^{2+} = 97 pm $\triangleq$ 0.97 Å; Co^{2+} = 78 pm $\triangleq$ 0.78 Å) compared with nickel, lithium can be easily deposited in lattice defects or in gaps in the nickel hydroxide structure.

The following advantages and disadvantages result from its addition to sealed sintered electrode cells (Table 4/3):

Table 4/3:
Effect of added lithium on the electrochemical behaviour of nickel hydroxide electrodes

Advantages	Disadvantages
1. Improved charging efficiency at high ambient temperatures (40 °C). The higher the lithium content, the greater the effect (17).	1. Reduced cell capacity during discharge at room temperature or below. The effect increases with the lithium concentration. 2. Increased swelling of the positive sintered electrode after prolonged charging and cyclic operation. 3. Increased oxidation of the nickel sintered electrode at high temperatures.

Because of the disadvantages listed above, lithium additive is only recommended for cells with sintered electrodes that are designed for special purposes. Should these cells be charged over a wide temperature range, including below 20 °C, then the charge current should be as low as possible. Besides the effect on the kinetics of the nickel hydroxide electrode, the lithium additive also adversely effects the electrolyte conductivity, notably at high discharge rates and at low temperature.

Elements and Compounds that are not to be Used in Sealed Nickel-Cadmium Cells

Of the series of cation- and anion-forming elements which cannot be tolerated in sealed nickel-cadmium cells the most important are iron (Fe), manganese (Mn), copper (Cu), and chromium (Cr), also nitrates, carbonates, chlorides, and a large number of organic compounds. The adverse effect of iron is that at the positive sintered electrode the oxygen overvoltage (section 5.2.6) is significantly decreased so that in the limiting case no oxidation of the nickel hydroxide (charging of the positive electrode) by the charging current results and hence no energy storage occurs; the charging current produces

only heat and oxygen. An iron content of 1% in the active mass of sintered electrodes causes a capacity loss of up to 30%! Therefore, all the structural components inside the cell which come into contact with the positive electrode must be free from iron, and any steel parts must be nickel plated with the coating as free from pores as possible. That applies to the carrier grid materials in the sintered electrodes at present in production (section 4.2.1), likewise for the electrode connectors and the cell case (chapter 7).

Manganese and copper are elements which are soluble in alkaline electrolytes and whose ions are oxidized at the positive electrode and reduced at the negative electrode. With manganese these reactions recur continually, so that the electrodes discharge themselves; the self-discharge rates of cells (section 5.6.2) then reach rates which are clearly unacceptable.

The self-discharge effect is not only limited to the elements mentioned; there is a further group of substances which can discharge nickel and cadmium electrodes. Nitrate ions, for example, belong to this group and they can enter the electrolyte during the manufacturing process (sections 4.2.1 and 5.6.2); many organic compounds behave similarly.

4.3.2 The Cadmium Hydroxide Electrode

4.3.2.1 Raw Materials and End Products During Charge and Discharge
Cadmium hydroxide is the active material in the negative electrode of the nickel cadmium battery. Cadmium oxide (CdO) also plays a part in the preparation of this electrode; it changes in aqueous alkaline electrolytes by absorbing water into cadmium hydroxide, thus:

$$CdO + H_2O \rightarrow Cd(OH)_2 \qquad [4/5]$$

Cadmium hydroxide is generally produced by two methods, one electrochemical, the other chemical. Electrochemically, the material is deposited by the action of an electric current passed through a solution containing cadmium ions; in the second the hydroxide is obtained from a cadmium salt solution (e.g. $Cd(NO_3)_2$-solution) by precipitation in the presence of sodium or potassium hydroxide.

$$Cd(NO_3)_2 + 2KOH \rightarrow Cd(OH)_2 + 2KNO_3 \qquad [4/6]$$
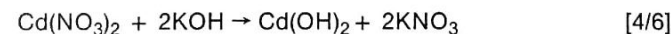
Cadmium hydroxide forms hexagonal crystals depending on the manufacturing conditions, the "cubic" (hexahedron) form (Fig. 4/11), or the "lamellar" form (Fig. 4/4). In the sintered electrode, for example, they can be easily determined under a scanning electron microscope.

Fig. 4/12:
Crystal size of metallic cadmium as a function of the number of cycles related to different charging currents
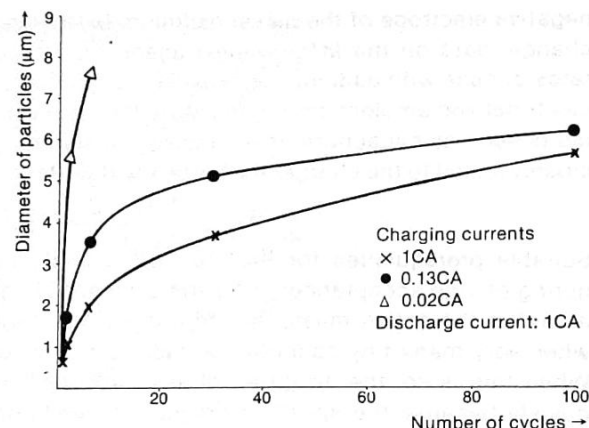
An increase in crystal size can also be caused by the number of charge/discharge cycles since the cadmium hydroxide ions ($Cd(OH_3^-)$) dissolved in the electrolyte can migrate. Depending on variations in concentration and charge they migrate from the negative electrode in the direction of the positive electrode. This phenomenon is more noticeable in cells with bulk of electrolyte, e.g. in vented nickel-cadmium batteries than in sealed batteries. In the worst case, it can cause metallic cadmium to build up in the separator or pass through it to the positive electrode. This leads to a soft short-circuit and to cell failure.

In addition, before the short-circuit can occur, the material accumulated in the peripheral layers of the electrode has an adverse effect on the electrolyte supply and hence on the current distribution. The outer zones contain, in the worst case, hardly any pores filled with electrolyte, and the interior of the electrodes has very little active material.

The following operating conditions will minimize the growth of metallic cadmium and cadmium hydroxide crystals, and hence improve the electrochemical behaviour of the negative electrode:

1. High charging current.
2. Low operating temperature.
3. Low ambient temperatures when the cells are stored for long periods.
4. Storage in the discharged condition.
5. Average or high discharge rates.

4.3.2.2 E.m.f., Capacity

The simplified reaction equation for charging and discharging of the Cadmium/Cadmium Hydroxide electrode is:

$$Cd(OH)_2 + 2e^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} Cd + 2 OH^- \qquad [4/10]$$
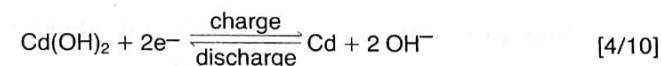
Using the free enthalpy $\Delta G = 156.24$ kJ/mol and the equation:

$$V_o = -\frac{\Delta G}{z \cdot F} \qquad [4/11]$$

the equilibrium potential for $a_{OH^-} = 1$ referred to the standard hydrogen electrode is

$$V_o = \frac{-156.24}{2 \cdot 96500} = -0.809 \text{ V} \qquad [4/12]$$

The storage capacity for complete charge (reduction) of the cadmium hydroxide amounts to 2 x 96.500 As for 146.4 g $Cd(OH)_2$, or 366 mAh/g $Cd(OH)_2$.

This capacity is the same as that stored during the initial charge of the sintered electrode, but during the first discharge this type of electrode will only achieve about 70% of the maximum theoretical capacity. For mass plate electrodes (e.g. button cell electrodes) in which the active mass is mixed with the conductive material, the corresponding capacity is about 60% when the electrodes are discharged at the 5 hour rate, i.e. 225 mAh/g $Cd(OH)_2$. The difference in the value for sintered electrodes can be explained by the different conductivities of the two types of electrode. Just as in the nickel hydroxide electrode, it has to be remembered that the specific capacity of the cadmium hydroxide electrode in the sintered cell is based only on the active mass and is 256 mAh/g $Cd(OH)_2$. The values for the electrodes are dependent on the weight of conductive material and the reinforcing of the electrode, and are correspondingly lower.

4.3.3 Cell Mechanisms
4.3.3.1 Charge and Discharge

The equations of the reactions for the positive and negative electrodes are difficult to formulate because the reaction products are affected by conditions in the manufacturing process. It is just as difficult to write an equation

for the overall reaction. In its simplest form, i.e. neglecting constitutional water and potassium ions in the nickel hydroxide hydrate crystal lattice, the following describes the reactions occurring during charge and discharge:

Positive electrode

$$2\,Ni(OH)_2 + 2\,OH^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} 2\,NiOOH + 2\,H_2O + 2e^- \quad [4/13]$$

$$V_o = +\,0{,}490\ V$$

Negative electrode

$$Cd(OH)_2 + 2e^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} Cd + 2\,OH^- \quad [4/14]$$

$$V_0 = -\,0{,}809\ V$$

Overall reaction

$$Cd(OH)_2 + 2\,Ni(OH)_2 \underset{discharge}{\overset{charge}{\rightleftharpoons}} Cd + 2\,NiOOH + 2\,H_2O \quad [4/15]$$

$$V_o = +\,0.490 - (-0.809) = 1.299\ V$$
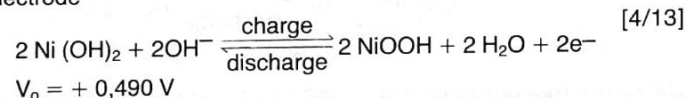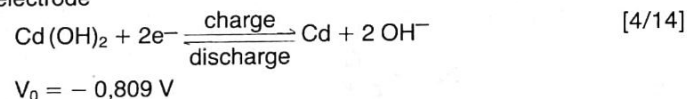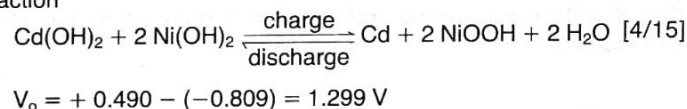
It is a characteristic of the alkaline system that in the overall reaction, the potassium hydroxide content of the electrolyte does not vary, but only small and, in practice, insignificant changes occur in the amount of water. The open-circuit voltage of the cells is independent of the potassium hydroxide concentration because the slope of the graph of voltage against pH is the same for both electrodes (see section 4.3.1.2, Nernst equation).

During charge, water forms at the positive electrode in addition to the charge product and causes dilution of the electrolyte in the immediate vicinity of the electrode. If the charging rate is low, the difference in concentrations between parts of the electrolyte can balance out, and the conductivity of the electrolyte overall remains unaltered. During high rate charge and discharge, differences in concentration in the electrolyte occur in the pores and on the surface of the electrodes and bring about a voltage drop or an overvoltage (21). At low temperatures the dilution can lead to freezing in the pores of one electrode, and to higher electrolyte concentration and precipitation of solids in the pores of the other.

4.3.3.2 Overcharge

Overcharge of the electrodes in a battery occurs when electrochemically active materials of zero charge acceptance are present in significant amounts. In such circumstances, there will be evolution of gasses at both electrodes. The positive electrode evolves oxygen according to the formula:

$$4\,OH^- \rightarrow 2\,H_2O + O_2 + 4e^- \quad [4/16]$$
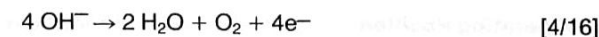
and hydrogen is evolved at the negative electrode:

$$4\,H_2O + 4e^- \rightarrow 2\,H_2 + 4\,OH^- \quad [4/17]$$

The equation for the overall reaction is:

$$2\,H_2O \rightarrow O_2 + 2\,H_2 \quad [4/18]$$

These reactions occur in vented cells from which the gasses so produced can escape. Equation [4/18] shows that water is extracted from the electrolyte, and with vented cells this has to be returned by topping up during maintenance periods.

The charge acceptance of the negative electrode is very efficient, i.e. the evolution of hydrogen at the cadmium electrode does not start until the electrode is practically fully charged.
This is explained by the high value of the hydrogen overvoltage for cadmium and the approximately 20mV more positive equilibrium potential of the cadmium/cadmium hydroxide electrode referred to a hydrogen electrode. The positive electrode is considerably less efficient. Evolution of oxygen starts anywhere between 10% and 70% of the fully charged capacity depending on charging current and temperature (section 5.2.6). Consequently, there is increasingly more oxygen than hydrogen produced during charge. These gasses are not evolved in stoichiometric proportions, so they cannot be recombined to water following equation [4/18], which is one of the chief disadvantages of the nickel-cadmium battery. Because of this, many attempts to make a sealed cell have not been successful.

4.4 Principle of the Sealed Battery

4.4.1 Disadvantages of Vented and, Advantages of Sealed Nickel-Cadmium Batteries

The vented nickel-cadmium battery has been manufactured on a commercial scale since the turn of the century and is today in a highly developed state. It is an ideal power supply for many applications. Its disadvantages are:

1. **Maintenance**
   It is required at regular intervals because during charge, water is decomposed in the electrolyte and the gasses thereby produced escape from the cell. This water must be continually replaced.

2. Operating Position
These cells can only be used in an upright position, otherwise highly caustic potassium hydroxide will escape.

3. Corrosive Gasses
During overcharge, the gasses evolved escape from the cell and carry along with them droplets of the caustic electrolyte which will have a corrosive effect on the surroundings.

4. Ventilation
The oxygen and hydrogen evolved during charging form an explosive mixture when present in certain proportions. During ventilation of the battery room, precautions must be taken that no explosive mixtures of these gasses can build up in ducting etc. (See VDE 0510) (22).

The disadvantages enumerated above can all be eliminated by a single solution:

Hermetic sealing to prevent loss of gas and electrolyte!

The efforts of several generations of scientists have been directed to achieving this objective; hence much effort has gone into solving the problem of how the gasses can be made to recombine and, therefore, rendered harmless. All efforts to bring about the recombination of

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad [4/19]$$

with the help of coils of platinum or palladium wire or with auxiliary electrodes have been unsuccessful. The chief causes are on one hand the low velocities of reaction of hydrogen oxidation at these auxiliary electrodes so that a continuous rise in gas pressure in the cell case is observed, on the other hand the gasses are not evolved in stoichiometric proportions so that equation [4/19] does not apply and hence no equalization of pressure can come about.

4.4.2 Oxygen Cycle During Overcharge of Sealed Batteries
At the end of the 1940's, Neumann, Dassler and other scientists discovered the principle on which all present day sealed nickel-cadmium batteries are based (23). They were able to prove that the negative cadmium hydroxide electrode is able to, during charge, recombine the oxygen evolving at the positive electrode at a sufficient rate. The rate at which this oxygen is "consumed" is dependent essentially on how quickly it can reach the negative electrode. This can be controlled by the parameters used in the design of the cell structure. The following parameters are conducive to a low gas pressure on the cell case:

— small spaces between electrodes
— large catalytically effective surface area of the negative electrode (i.e. sintered electrodes are better for this purpose than mass plate electrodes)
— highly porous negative electrode

— minimum amount of electrolyte
— low electrolyte concentration
— highly porous separator, e.g. mesh or web separator
— high cell temperature

The amount of electrolyte and the porosity of the separator are chosen so that the separator is only partly filled with electrolyte; i.e. all the electrolyte is held in the electrodes and separator. Consequently, there is in a sealed battery no "free" electrolyte in the head-space which can escape should the cell develop a leak.

When the parameters stated above are satisfied then oxygen at the three phase boundaries (solid, liquid, gaseous phases) can be reduced according to either of the two following equations:

1. By oxidation of the cadmium (chemical reaction):

$$Cd + \tfrac{1}{2}O_2 + H_2O \rightarrow Cd(OH)_2 \qquad [4/20]$$
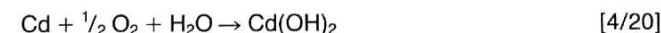
2. Electrochemical reduction:

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2\,OH^- \qquad [4/21]$$

Equation [4/21] ignores the fact that the reaction generally takes place in two stages.

Bode, Dehmelt and v. Döhren (24, 25) have shown that the electrochemical reaction is not linked to the presence of cadmium, but that for example with sintered electrodes it occurs preferentially with metallic nickel, and that it is a first order reaction which depends on oxygen pressure. According to measurements made by these authors, 73% of the oxygen was electrochemically reduced, whereas only 27% was reduced by chemical reaction with cadmium.

These parameters should be the aim if the cell is to be charged at high rates, i.e. when one is designing a "fast charge" cell. However, it is important to remember that by excessive application of these parameters to obtain good gas recombination characteristics, e.g. by using a small amount of electrolyte of low concentration, other characteristics of the battery can be adversely affected, particularly the capacity at high current or performance at low temperatures.

4.4.3 Overcharge Protection
It was stated in section 4.4.2 that the oxygen evolved at the positive electrode during charge and overcharge can be recombined at the negative electrode

after suitable structural arrangements have been incorporated into the design. To this end, the proportions of each electrode can be so designed that complete charge of the cadmium electrode does not occur and consequently the formation of hydrogen by decomposition of water is prevented; consumption of hydrogen by its oxidation at the positive electrode would proceed so slowly that the reaction would have no significant effect in the cell.

In sealed cells, therefore, the capacity of the negative electrode is oversized with respect to the positive. The fraction by which this electrode is larger than the positive is described as the negative "charge reserve", and negative "discharge reserve" respectively (Fig. 4/13). The negative charge reserve consists of cadmium hydroxide and prevents evolution of hydrogen in the cell. The negative discharge reserve is formed from metallic cadmium and at high discharge rates provides an easily usable electrochemical reserve capacity.

Fig. 4/13:
schematic diagram of the capacity distribution within a cell
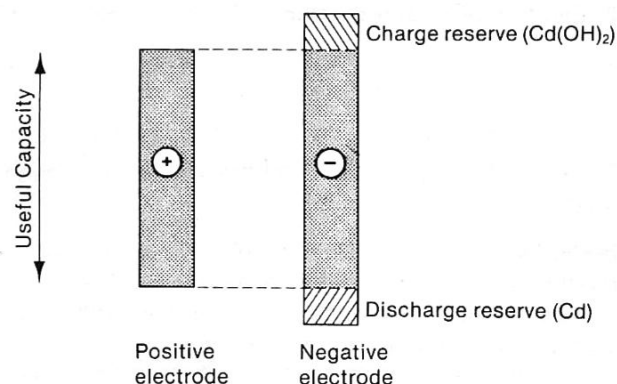
The negative charge reserve should be of such a size that it equates to the electrochemical equivalent of the oxygen stored in the cell under its designed working conditions, because on overcharge the oxygen pressure steadily increases. The oxygen consumption proceeds according to equations [4/20] and [4/21] until such time when equilibrium is reached, which depends on the operating conditions and the mechanical structure of the cell. In equilibrium, the total charging current at the negative electrode is then used for oxygen reduction. The electrode cannot then be charged further, so that the voltage of the cadmium/cadmium hydroxide electrode remains constant and no hydrogen is evolved.

In order to give sealed batteries a long useful life, there must, in addition, be a part of the charge reserve set aside for:

— oxygen loss through separator oxidation
— loss of gas by diffusion
— oxidation of conductor material at the positive electrode (more relevant in cells with sintered electrodes, and cells designed to achieve maximum life).

Even with a very small gas leakage from a cell, the effects can be so grave that within a few months of service, the total charge reserve is consumed; after that hydrogen is evolved during overcharge. Because the evolution of gas is significantly greater than the rate of leakage, the internal pressure will build up until it exceeds the permitted maximum for the cell, and gas must be released through a safety valve. After this, the cell will always start evolving hydrogen under the same operating conditions and consequently the electrolyte amount is continuously decreased. The cell no longer works reliably as a sealed cell and the end of its useful life is in sight! The following example illustrates how strongly a tiny gas leak can affect the reliability of the cell:

When a leakage rate of 0.026 cm^3 oxygen per hour occurs under normal operating conditions, after one year it equates to a reduction in the negative charge reserve of about 1 Ah. A charge reserve of this order of magnitude, for example, is built into a cylindrical 7 Ah sintered cell. With the assumed leakage rate, after about one year of service, the cell will no longer function as a sealed cell and will fail.

For a nickel cadmium battery which is overcharged on purpose for a prolonged period and which must continue to function reliably, provision must be made for an increased negative charge reserve. The amount will depend on the maximum internal pressure of the cell as well as on the volume of free gas.

4.4.4 Protection against Polarity Reversal During Overdischarge

Present day sealed nickel-cadmium batteries are very reliable and are protected against polarity reversal, i.e. the cells are made in such a way that no damage can result even when there is an occasional polarity reversal. Polarity reversal of individual cells in a battery is usually the result of deep discharge and is unavoidable because the capacities of the individual cells are, in practice, slightly different. Capacity variation between cells will, in time, occur even when cells are matched and built into a battery, because self-discharge and all the other factors which determine the useful life of a battery (section 5.6.3) can vary from one cell to another.

In banks of batteries on discharge, the cell with the least capacity will be the first to reverse its polarity, i.e. its voltage is the first to fall to zero, then a

voltage of the opposite polarity appears across the terminals. As a consequence of polarity reversal, oxygen will evolve at the cadmium electrode, which in a cell without protection against polarity reversal leads to an unacceptable rise in pressure so that either the case is punctured or the safety valve blows (Chapter 5). In the interest of maximum life and reliability, it is essential that gas does not escape through the safety valve. VARTA nickel-cadmium cells contain material which consumes the oxygen evolved should polarity reversal occur. The reaction mechanism is similar to that occurring during overcharge.

Polarity reversal protection is achieved by a modification to the cell's active materials: the positive electrode contains an additional accurately pre-determined amount of cadmium hydroxide — termed, "antipolar mass".

Fig. 4/14:
Schematic diagram of voltage and gas pressure changes during polarity reversal

The significance and effectiveness of the „antipolar mass" can be seen in Fig. 4/14. The capacities of the positive electrode (NiOOH when charged, and $Ni(OH)_2$ when discharged) and the negative electrode (Cd and $Cd(OH)_2$ respectively) are shown as shaded rectangles. The size of the positive electrode is increased by the antipolar mass, and the negative electrode by the charge and discharge reserves. The voltage during discharge is shown by the graph at the bottom of Fig. 4/14. If the capacity of the positive electrode of a cell within a battery is totally consumed during a discharge cycle, then the voltage falls through zero and reverse polarity occurs. Whilst the current still flows, the antipolar mass is charged, i.e. the cadmium hydroxide in the positive electrode is reduced to metallic cadmium. The potential of the discharged nickel hydroxide electrode adjusts itself to the cadmium/cadmium hydroxide potential, whilst the potential of the negative electrode stays constant until the useful capacity and the discharge reserve are used up. After that, the potential falls abruptly until oxygen starts to evolve at this elec-

trode. The evolved oxygen moves across to the opposite electrode and discharges the partly charged antipolar mass in a similar manner to the overcharge mechanism already described. As long as the gas consumption process continues, the initial pressure in the cell will fall to a stable limited value. That means, in this condition the polarity reversal can continue, without damage occurring or electrolyte being consumed. By correctly designing the amount of the negative discharge reserve and the antipolar mass, it is possible to ensure that no hydrogen is evolved in the cell and that any oxygen evolved will be safely recombined.

Consequently, nickel-cadmium batteries provided with reverse polarity protection are also protected against misuse for discharges up to the rated discharge current (see definition in section 5.1.1).

5. Electrical Properties of Sealed Nickel Cadmium Batteries

5.1 Discharge Mechanisms

5.1.1 General Discharge Characteristics

When the terminals of a cell or one of several cells making up a battery are connected via external leads to a load, then an electric current flows between them. In this way, chemical energy stored in the cell is transferred to the load as electrical energy.

The amount of electricity that can be taken from the battery is known as the „capacity". Its amount depends partly on the conditions of discharge, particularly the amount of current, and on the ambient temperature. The capacity is measured as the product of the current supplied, in ampères (A), and the period of the discharge measured in hours (h). The actual useful capacity is determined by the discharge voltage characteristic. The voltage rating of a sealed nickel-cadmium cell is 1.2V. On the other hand, the off-load or open-circuit voltage, as measured across the terminals, can be between 1.28V and 1.35V, depending on the duration of storage.
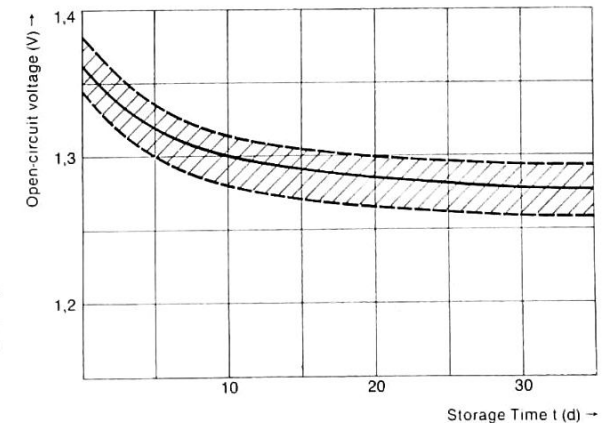
Fig. 5/1:
Open-circuit voltage of sealed cylindrical cells as a function of storage time at room temperature

The on-load voltage falls progressively during discharge. A typical discharge characteristic is shown in Fig. 5/2.
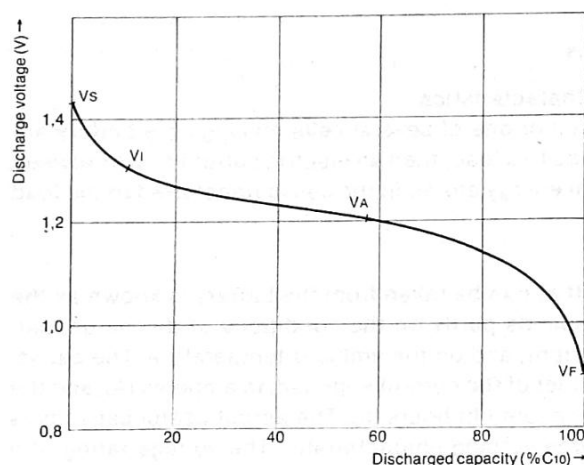
Fig. 5/2:
Voltage characteristic of a sealed nickel-cadmium battery as a function of the discharged capacity, at room temperature

The following important points on the discharge voltage characteristic can be stated:

— The starting voltage, V_S:
  The voltage measured at the moment the load is applied. It is not of great significance because its value is greatly dependent on the circumstances of the previous period of storage time.

— The initial voltage, V_I:
  Terminal voltage which is measured after 10% of the useful capacity has been consumed under the discharged conditions specified.

— The average voltage, V_A:
  Average value of all voltages measured over the total discharge period; it is approximately the voltage after 55% of the useful capacity has been consumed.

— The final voltage, V_F:
  The end-of-discharge voltage; if this is not mentioned in the specification, it varies from 230mV to 330mV below the initial voltage V_I.

The final voltage as defined above determines the time factor for capacity rating purposes.

The storage capacity of some sealed mass plate cells is specified in terms of the „10-hour capacity" (C_{10}) and is measured in Ah or in the smaller unit, mAh. This is the capacity which can be supplied by the battery over a period of 10 hours.

Capacity (Ah) = discharge current (A) x period of discharge (h).

The corresponding nominal current is defined as the „10-hour current" ($C_{10}A$). It is that value of current which will discharge the battery at 20 °C ambient temperature in exactly 10 hours down to a specified final voltage of 1.1V For cells with sintered electrodes and some mass plate cells, the capacity is given as the 5-hour capacity (C_5). The „5-hour current" (C_5A) discharges this cell down to a specified final voltage of 1.0V after 5 hours. The energy extractable from the cell (available power) is calculated as the product of the storable capacity and the average discharge voltage. It is measured in watt-hours (Wh).

5.1.2 Factors that Determine Capacity and Voltage Characteristics
The capacity of a cell is not constant. On the contrary, it depends on a wide variety of factors. Thus, the extractable capacity is affected by the type of construction, the manufacturing methods, and physical cell parameters on one hand, and on the operational parameters on the other.

5.1.2.1 Structural Parameters that Determine Capacity and Voltage
The discharge characteristic of a cell is to some extent determined by its internal resistance. This has an important control over the terminal voltage characteristic at a given load and hence over the useful capacity to a specified final voltage (section 5.3). The internal resistance is essentially a function of the structural parameters of the cell.

The most important parameters are:
— the type of electrode materials used (mass plate or sintered electrode)
— porosity and surface area of the active mass
— geometry of electrodes (current distribution)
— distance between electrodes
— amount and concentration of the electrolyte (conductivity)
— type, thickness, porosity and electrolyte absorption of the separator
— cross-section area of current collectors and contact resistance of its connections.

Sintered electrode cells have particularly low internal resistances. The high proportion of metallic conductive material in the form of a highly porous sintered nickel cake ensures good capacity and voltage characteristics. They

are better than those of mass plate cells (e.g. button cells) for the same discharge conditions.

Fig. 5/3 shows the relationship between the useful capacity and the discharge current for mass plate and sintered cells. The figure also shows the effect of a reinforced current collector system in reducing the internal resistance.
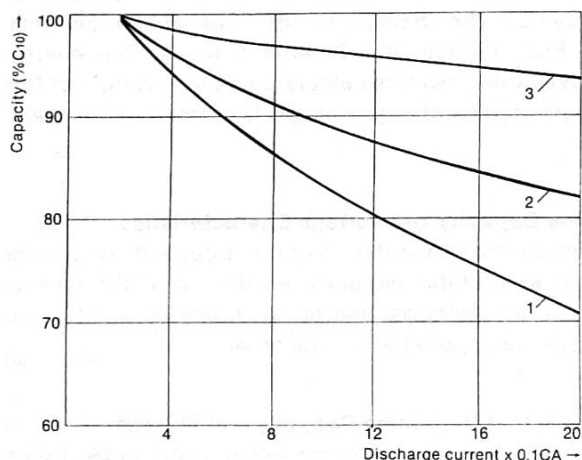
Fig. 5/3:
Capacity as a function of discharge current for various structural parameters in nickel-cadmium cells
1: Button cells type DKZ with mass plate electrodes
2: Cylindrical cells type RS with sintered electrodes
3: Cylindrical cells type RSH with reinforced current collectors

Besides of these purely structural parameters, the electrolyte is of great importance. Low electrolyte concentrations are the cause of high ohmic resistance. The on-load terminal voltage is reduced by the internal voltage drop and this results in a lower available capacity.

Fig. 5/4 shows the influence of the potassium hydroxide concentration on the electrolyte conductivity. The curves are temperature-dependent and pass through a well defined maximum within a concentration range of 1.25 to 1.30 kg/l.

Most manufacturers, therefore, use an electrolyte concentration of about 1.30 kg/l, i.e. concentrations which lie in and around the peak electrical conductivity.
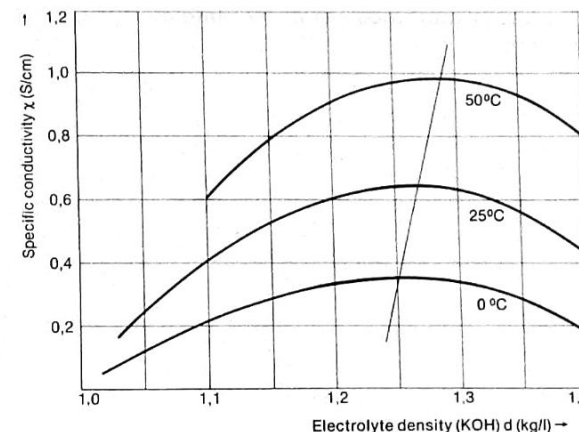
Fig. 5/4:
Conductivity as a function of electrolyte density at various temperatures

It is important to remember that changes in electrolyte concentration occur inside the electrodes during discharge. Hence at high discharge current densities, the capacity and voltage characteristics are significantly affected by the concentration and the amount of the electrolyte held in the pores of the electrodes.

The operational usefulness of sealed cells also depends on the electrolyte concentration at low temperatures. Extreme low temperatures can lead to ice crystals forming on the electrodes. Theoretical reasons support the manufacturers' choice of electrolyte densities of 1.27 to about 1.32 kg/l for reliable prevention of ice formation between —40 °C and —70 °C (Fig. 5/5).

According to the simplified equation for the cell reaction

$$2\,Ni(OH)_2 + Cd(OH)_2 \xrightarrow{\text{Charge}} 2\,NiOOH + Cd + 2\,H_2O \qquad [5/1]$$
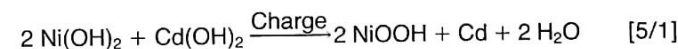
water is produced during charging. This causes dilution of the electrolyte. This causes about 0.02 kg/l drop in density only. A concentration gradient can be observed within the cell because in the immediate vicinity of the negative electrode there is maximum water production during charge. Hence, some variation in electrolyte density can be observed over microscopic distances, which at very low temperatures can at times lead to ice formation and hence to a rapid rise in internal resistance.
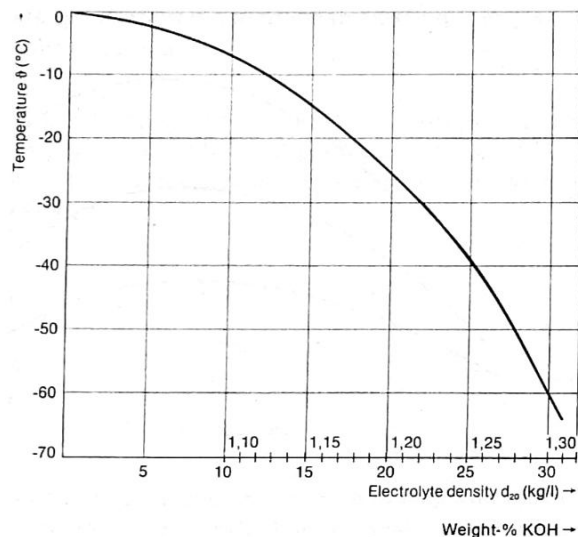
Fig. 5/5:
Ice formation in potassium hydroxide as a function of temperature for various electrolyte densities (wt. %)
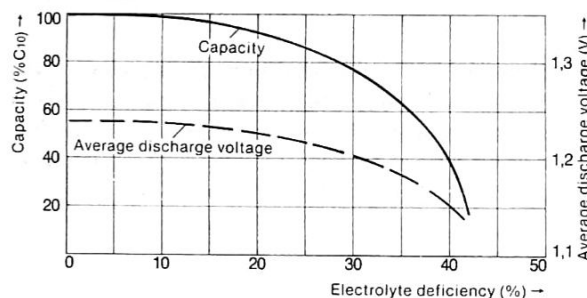
Fig. 5/6:
Extractable capacity and average discharge voltage as a function of electrolyte deficiency in sealed cylindrical sintered cells type RS during discharge at 1CA, room temperature

The amount of electrolyte contained in the cell also has a significant effect on the capacity and voltage characteristics. Too little causes a loss of capacity, too much leads to problems during charge.

Thus for every type of cell, there is an optimum amount of electrolyte and this must be carefully calculated to achieve the required charge and discharge characteristics.

Fig. 5/6 clearly shows the decrease in extractable capacity and in the average discharge voltage caused by electrolyte deficiency.

5.1.2.2 Operational Factors that Determine Capacity and Voltage Effect of Discharge Rate

The extractable capacity is dependent on the load. The higher the discharge current, the greater the slope of the discharge characteristic and the greater the change in voltage during discharge; the useful capacity is also less.

Fig. 5/7 gives the principal voltage characteristics for a sealed cell at increasing load currents. The discharge characteristic is flatter at smaller loads.
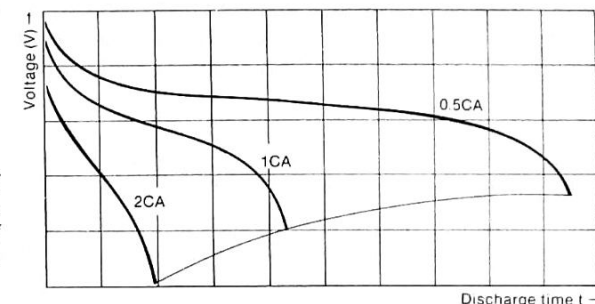
Fig. 5/7:
Voltage characteristic of sealed nickel-cadmium batteries as a function of discharge time at various discharge currents

Fig. 5/8 gives representative capacity and voltage characteristics of sealed cells for loads between 0,2CA and 2CA. Depending on whether button cells with mass plate electrodes, cylindrical or rectangular cells with sintered electrodes, or special cells for extreme conditions are concerned, so will the capacity and voltage characteristics have more or less increased slope at increasing load currents.

The example given shows the characteristics of two types — button cells in the DKZ series, and the standard cylindrical sintered cell type RS.
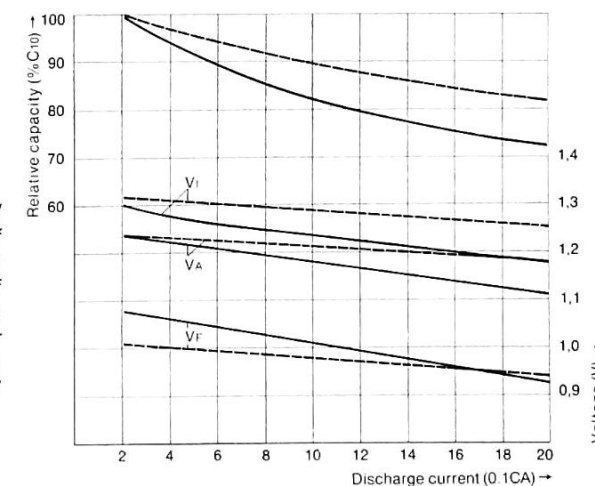
Fig. 5/8:
*Relative capacity and voltage characteristics of sealed nickel-cadmium batteries as a function of different discharge rates at room temperatures for mass plate button cells type DKZ and cylindrical sintered cells type RS;
DKZ ————, RS - - - -*

Effect of Temperature

The temperature during discharge has a very noticeable effect on the extractable capacity of sealed cells. The specific resistance of the electrolyte rises sharply at low temperatures. At —20 °C, it has risen to about three times that at 20 °C. Thus the internal resistance of the cell rises quickly at low ambient temperatures, which, in turn, reduces the extractable capacity. The drop in capacity is less pronounced with sintered electrode cells (cylindrical sintered cells type RS or rectangular sintered cells type SD) than with mass plate cells (e.g. button cells type DKZ) due to the generally lower internal resistance resulting from the high proportion of conductive material forming the sintered grid. This relationship is shown in Fig. 5/9.
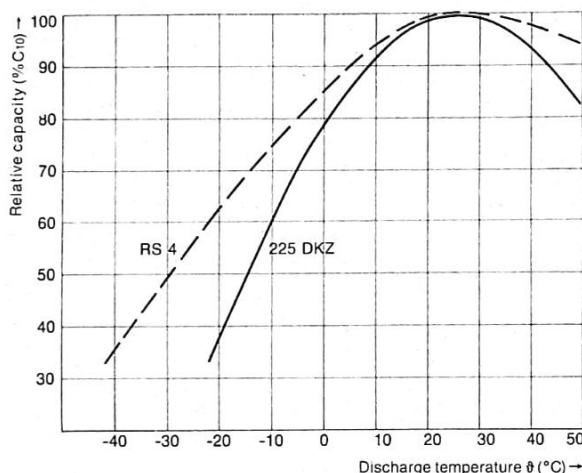
Fig. 5/9:
Relative capacities referred to effective capacity at $\vartheta = 27\,°C$ ($\triangleq 100\%\ C$) as a function of the discharge temperature at discharge at 1CA for cells type RS 4 and 225 DKZ (Charge: 14 h, 0.1CA, charging temperature $\vartheta = 27\,°C$)

SD cells and RS cells can, therefore, also be used at temperatures from —20 °C to about —45 °C, but mass plate cells (e.g. button cells) cannot be used in this temperature range.

The drop in capacity and voltage at low temperatures is more pronounced at high load currents. Fig. 5/10 gives the extractable capacity and the average discharge voltage of button cells at discharge currents of 0.2CA, 1CA and 2CA over the whole temperature range.

Effect of Charging Conditions

The relationships so far discussed apply only for fully charged cells. They must be charged at the specified current in normal ambient temperatures, paying attention to the charge factor specified (section 5.2).

Fig. 5/10:
Effective capacities and average discharge voltages as a function of discharge temperature for various discharge currents; mass plate button cells type 225 DKZ
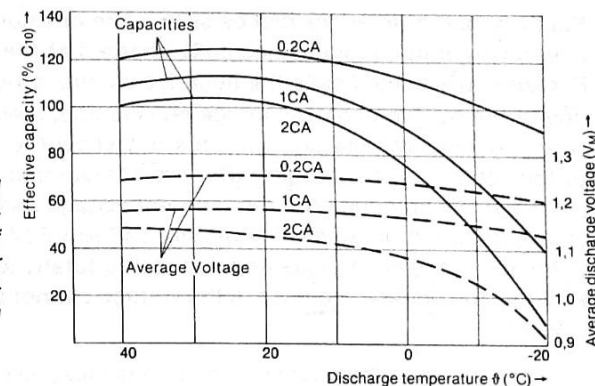
Because the charge acceptance of cells is a function not only of charging current density but also of temperature, the relationships are complex when charge and discharge are performed at very high or low temperatures. This topic is considered in more detail later.

5.2 Charging Characteristics

5.2.1 Voltage Characteristic During Constant Current Charge
Two charging methods can, in general, be used for sealed batteries:

1. Charge at constant current (I-characteristic).
2. Charge at decreasing current, i. e. with W-characteristic using W-charger (see section 9.3)

Charging at constant voltage, (V-characteristic) as often used for vented cells, cannot be used for sealed cells.

Charging is generally carried out at the specified current, i.e. at the 10-hour rate, 0.1CA (section 5.1.1).

In order to achieve a complete charge of normally discharged cells or batteries a charging time of 14 hours is required. When lower charging currents are used, then the charging period must be correspondingly longer; at higher rates it is, of course, shorter.

The total amount of current stored is the product of the constant value of the current used and the total charging time. A factor of about 140% must be used related to the nominal capacity for recharging under the above mentioned charging conditions. Hence, the concept of „charge factor" of 1.4 is calculated, i.e. for full charge, 1.4 times the previously extracted capacity must be re-charged.

Fundamental differences can be seen when one compares the voltage characteristics of open and sealed cells charged at the nominal rate (Fig. 5/11). Because with sealed cells the negative electrode never reaches full charge, due to the built-in negative charge reserve and, therefore, never reaches the corresponding voltage level, it does not show the distinct rise of terminal voltage at the end of charging which is characteristic of vented cells. During charge at the nominal rate, the terminal voltage rises, according to the type of cell construction, to a value of only 1.46 to 1.53V. A characteristic feature of full charge, gassing (gassing voltage) is totally absent in sealed cells. In addition, the gradual increase in the voltage cannot be used to switch off the charger.

On these grounds, the charging conditions must be carefully arranged to suit the type of sealed cell.
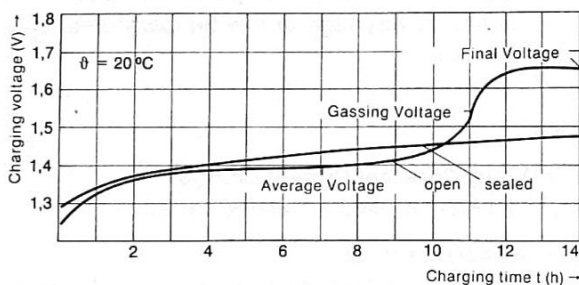
Fig. 5/11:
Charging voltage characteristic as a function of charging time at nominal charging current 0.1CA for vented and sealed nickel-cadmium cells at room temperature

5.2.2 Side Reactions During Charge of Sealed Cells
As with vented cells, side reactions are observed during charge and particularly during overcharge of sealed cells. Whilst, however, with carefully designed cell balance, the charge reserve in the negative electrode in sealed cells normally prevents the evolution of hydrogen, after charging to about 70% of full charge oxygen appears at the positive electrode, evolving slowly at first, then at an increasing rate as the charge continues:

$$2\,OH^- \rightarrow \tfrac{1}{2}\,O_2 + H_2O + 2e^-$$ [5/2]

Therefore, during charge there is a build up of gas pressure inside the cell. Fig. 5/12 shows the voltage and pressure relationship of a sealed sintered cell as a function of the amount of charge current. It is apparent that the cell pressure, relative to a certain state of charge, increases with charging rate. The pressure is primarily dependent on the rate of charge or overcharge, on the ambient conditions, and particularly on the structural parameters of the cell.
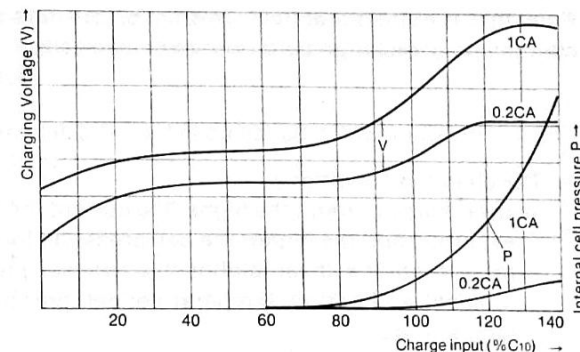
Fig. 5/12:
Charging voltage and pressure characteristics as functions of current stored for sealed nickel-cadmium batteries

The oxygen formed at the positive electrode during charge and overcharge is reduced by chemical and electrochemical means at the negative electrode at a rate depending on the increasing pressure:

$$2\,Cd + 2H_2O + O_2 \rightarrow 2\,Cd(OH)_2$$ [5/3]

$$O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$$ [5/4]
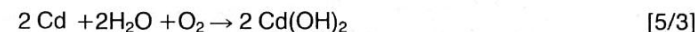
If the quantities evolved and reduced per unit time are equal, then an equilibrium pressure is maintained within the cell which is directly proportional to the charging current. If, in this overcharge condition, there is no further increase in pressure, even during continued charging, the cell is said to be safe against overcharge.

The rate of oxygen reduction depends primarily on the rate at which it is transported to the surface of the negative electrode. The path can be via the head-space in the cell or through the electrolyte. If the gas transport process is essentially one of movement of dissolved oxygen by diffusion through the electrolyte, the following linear relationship for equilibrium proposed by H. B. Lunn and J. Parker (26) applies:

$$K = \frac{I}{P} = 4 \cdot F \cdot S \cdot D \cdot \frac{A}{\delta}$$ [5/5]

in which
K = reaction velocity coefficient
I = value of the overcharge current
P = partial pressure of oxygen
F = Faraday constant
S = coefficient of oxygen solubility
D = diffusion coefficient for oxygen
A = total surface area of the negative electrode
δ = diffusion layer thickness

From this, it follows that the following factors have a controlling effect on the charge and overcharge behaviour of sealed cells.

The gas pressure which builds up in the cells depends on:

1. The charging conditions,
   — overcharge current: the higher the current the greater the rate of oxygen evolution and the higher the cell pressure; for nominal and high charge rates, there is a linear relationship between pressure and current.
   — ambient and battery temperature: cell pressure increases with falling temperature

2. The important structural parameters,
   — density of electrolyte: this determines the oxygen solubility; the higher the concentration of the electrolyte the higher the oxygen pressure.
   — the amount of electrolyte: insufficient electrolyte leads to large exposed electrode surfaces.
   — type and size of the electrodes.
   — electrode porosity, i.e. the actual electrode surface area.
   — the amount of negative charge reserve.
   — permeability of the separator to gasses.

3. The major geometrical dimensions
   — the packing density of the electrode assembly (pressure increases with increasing packing density).
   — internal dimensions of the case.

It is thus easy to see that the charging conditions are not the same for all types of cell, or can even be varied at will. The charging rates are dependent on cell type and this controls the limits of the charging time. Basically, the charging conditions as laid down by the battery manufacturer, should be followed closely. This is mostly a 7- or 14-hour charge at the nominal current, also known as the 5-hour and 10-hour current respectively. By conforming to these specifications, occasional overcharge over one or several days does not have any adverse effects. Accelerated charge at high currents, or fast charge (charging within 1 hour or less) on the other hand demands different types of cell construction and charging methods (section 9.3).

Fig. 5/13 shows how cell construction and geometry affects the pressure characteristic. In this figure, the cell pressure during charge for sintered cells is plotted against charging current density. In one case, the cell was a rectangular type in the series SD fitted with interleaved sintered electrodes, in the other the cell was a cylindrical sintered type RS with rolled electrodes. The overcharge factor in both cases was 1.3. An improvement in gas recombination is noticeable with rectangular cells, brought about by easier penetration

of the electrode structure and a different type of separator; this is indicated by the significantly lower pressure for the same charging current density and the same overcharge factor.

Fig. 5/13:
Internal cell pressure as a function of charging current density at an overcharge factor of 1.3 for sealed nickel-cadmium cells with sintered electrodes, series RS and SD at room temperature
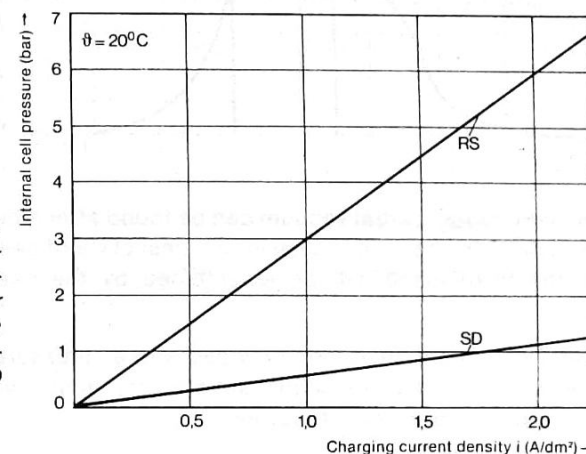
When the charge or overcharge of a sealed cell has finished and if the recommended charging rate has been followed, no harmful hydrogen pressure will have built up (section 5.2.4), then the pressure in the head-space falls exponentially as the result of continued chemical reduction of oxygen, according to the expression given by Lunn and Parker:

$$P = P_0 \cdot e^{-\frac{t}{\tau}} \qquad [5/6]$$

in which
P = pressure at time t
Po = initial pressure
t = time of the observation
τ = time constant

which is determined from

$$\tau = \frac{V}{RT} \cdot \frac{1}{SD} \cdot \frac{\delta}{A} \qquad [5/7]$$

in which

V = volume of head-space in the cell
R = gas constant
T = absolute temperature

The overall pressure characteristic of a sealed cell during charge, overcharge and storage on open-circuit is given in Fig. 5/14.
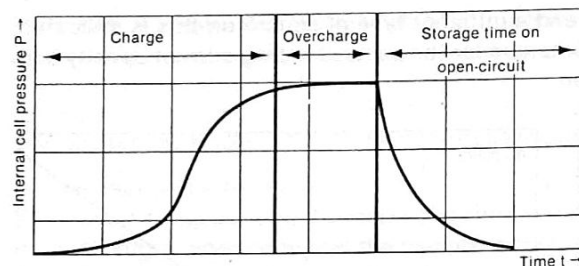
Fig. 5/14:
Internal cell pressure characteristic as a function of time for sealed nickel-cadmium cells during charge, overcharge and storage

In many cases, partial vacuum can be found after a period of storage, or after complete discharge because in the ideal state of cell balance all the oxygen in the head-space will be recombined by the cadmium in the negative electrode.

VARTA cells are, therefore, provided with a „pressure reserve", which keeps the working pressure within satisfactory limits when the recommended charging conditions are followed.

5.2.3 Charging Voltage Characteristic as a Function of Current and Temperature

The charging voltage characteristic during charge is a function of the charging current. Fig. 5/15 shows typical charging characteristics for sealed cylindrical sintered cells. Initially, the curves are nearly parallel. After charging to about 60—70% capacity, the curves diverge as the charging current increases. When the charging voltage and charging time are not controlled, then at high charging rates, problems will occur due to exothermic gas recombination reaction in the region of full charge. Due to the negative temperature coefficient of the charging voltage, there will be a fall in voltage on continued charging.
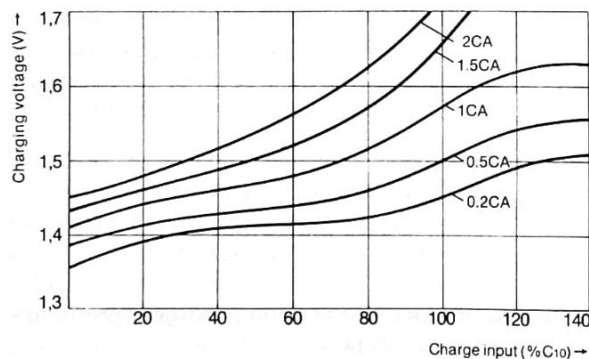
Fig. 5/15:
Charging voltage characteristic as a function of the current stored for cylindrical sintered cells type RS at various charging currents

Fig. 5/16 shows the effect of varying the ambient temperatures on the charging voltage characteristic. At low temperatures, critical voltage values are reached considerably earlier than under normal ambient conditions. Ambient conditions, charging currents, and cell type must, therefore, be matching.
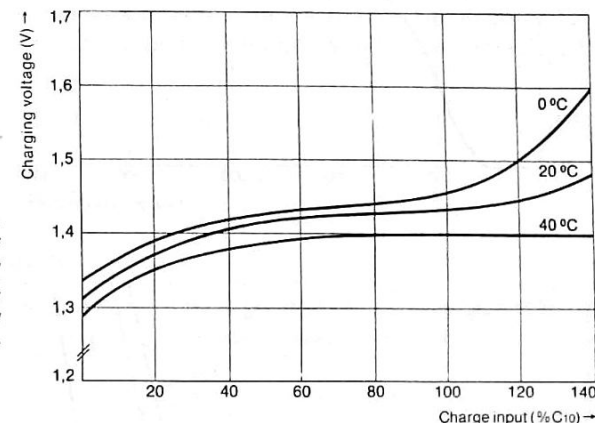
Fig. 5/16:
Charging voltage characteristic as a function of current stored for sealed nickel-cadmium cells at various temperatures and with the same charging current

5.2.4 Behaviour of Sealed Cells During Overcharge

Cells with a sufficiently large charge reserve can be safely overcharged (section 4.4.3). They are designed to be charged over prolonged periods at the appropriate current without risk of damage. This current is normally the 10-hour current (0.1CA) for mass plate cells, and, depending on the type of construction, the 5-hour (0.2CA) or 10-hour (0.1CA) with sintered cells. There will be no damage caused during overcharge at the nominal rate. Only frequent overcharging which goes far beyond the fully charged state of the cells, will have the effect of reducing the useful life. Mass plate cells (e.g. button cells) are more sensitive in this respect. This is also the reason why higher rates can be used for continuous charging or trickle charging (section 9.3) sealed sintered electrode cells.

In order to avoid excessive pressure rise in the cells, the recommended charging rates should not be exceeded. Sintered electrode cells are more suitable for charging with high currents for short periods. For this purpose, charging currents of up to 0.3CA can be used without the need for timing the charge duration, and without the need to ensure that the cells are fully discharged. Full charge can, therefore, be reached within 4.5 hours.

Fig. 5/17 shows the average pressure characteristic of a cylindrical sealed cell of 500 mAh capacity (500 RS) as a function of the charge input. Under these conditions, a steady state of pressure will occur. Thus, VARTA permits for this type of cell an overcharge at 0.3CA for up to two weeks.
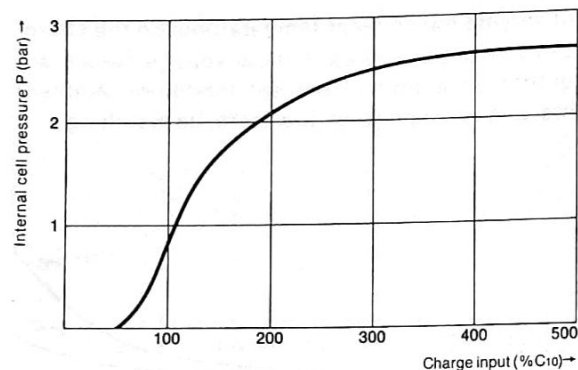
Fig. 5/17:
Internal cell pressure as a function of stored current for a cylindrical sintered cell type 500 RS charged at 0.3CA, room temperature
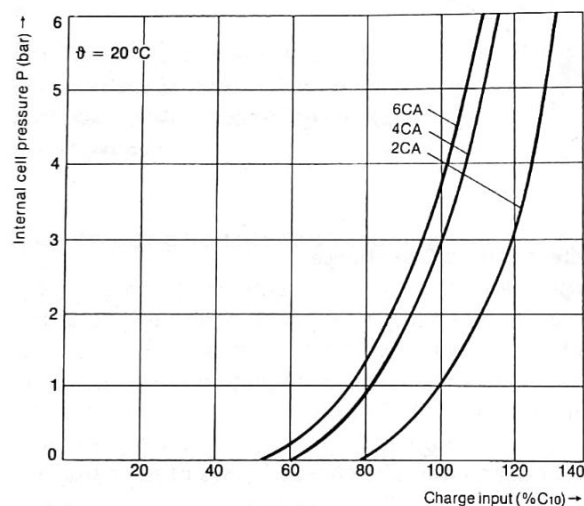
Fig. 5/18:
Average pressure characteristic as a function of charge input during fast charge of a sealed cylindrical sintered cell type 500 RS at 2CA, 4CA and 6CA at room temperature

When fast charge techniques are employed and the charge time is reduced to an hour or possibly even a few minutes, the relationships become very complex. In these circumstances, pressure equalization never occurs but the pressure rises steeply. Any overcharge will, therefore, bring about a pressure which, dependent on charge rate and the physical proportions of the cell, can cause distortion of the case and possibly cause the safety vent to operate.

Fig. 5/18 shows the average pressure increase curves which were obtained during charge of a 500 RS cylindrical cell at 20 x to 60 x the rated charging current. It is obvious that, for charge rates of this order, the charge time must be limited to avoid irreparable damage to the cell. Certain cell types have been designed for excessive overcharge applications (e.g. the VARTA RSX series).

During charge and overcharge of sealed cells, gas equilibrium is established so that the oxygen evolved at the positive electrode is consumed at the same rate at the negative plate. Because this gas recombination process is by nature exothermic, overcharging is accompanied by a rise of the cell's temperature, particularly at high charge rates. This heat is additional to the resistive heating caused by the cell's internal resistance and the two account for the total energy transferred during the overcharge period. This immediately leads to the expression

$$Q = 3.6 \cdot V \cdot I \cdot t \qquad [5/8]$$

Q = heat transferred (kJ)
V = end-of-charge voltage (V)
I = overcharge current (A)
t = period of overcharge (h)

An effective reduction in the amount of heat generated can only be achieved by significant reduction of the charging current, and possibly by shortening the overcharge period.

Cells of the standard design, e.g. button cells in the DK and DKZ series, standard cylindrical or rectangular sintered cells in the RS or SD series have a relatively high resistance when compared with the VARTA special series (RSH and RSX), which are designed for high charge/discharge currents. In particular, overcharging at rates of 20 x the rated current and above, will lead to case temperatures above those recommended. Besides a marked reduction in the charging efficiency, permanent damage can be the result.

Generally speaking, both thermal and pressure equilibrium are achieved during each charging cycle, and the heat generated is fully radiated via the case. In consequence, heating depends to a great extent on the cell dimensions, i.e. on the ratio between heat radiating surface to the cell capacity. Smaller cells (below 1Ah) with relatively large case surface areas can, therefore, be safely overcharged at 10 x the rated current without permanent damage due to excessive heating. On the other hand, with cells of capacities above 25 Ah, the heat generated by charging at twice the nominal rate cannot be radiated quickly enough. Special charging methods are, therefore, employed for cells of 25Ah and above.

5.2.5 Behaviour of Cells During Irregular Charging and Mishandling

The voltage, pressure and temperature characteristics show that overcharging of sealed cells is only possible at the specified rate, these rates being limited by the mechanical ability to withstand the internal pressures involved. In order to avoid permanent damage during fast charging, it is necessary to limit the charging time by suitable methods, e.g. time switches or voltage limits (sections 9.3 and 9.4).

Cell voltages, up to approximately 1.55V, will occur when trickle charging or when charging at higher rates for fixed periods and the internal pressures which arise are largely reversible. During periods of rest or discharge, oxygen recombination takes place. The internal pressure is thereby rapidly reduced. At increased charging rates, however, the degree of irreversibility increases. If the specified charge rates are exceeded, then during the subsequent discharge, higher residual pressure will occur, which is attributed to evolution of hydrogen at the negative electrode during charge (section 4.3.3.2, formulae [4/16] to [4/18].

Hence, the cell has an initial internal pressure at the start of the next charging cycle. With repeated abusive charging, the pressure can sometimes cause mechanical failure within a cell, or to the operation of the safety vent.

A table of possible mishandling and the consequences is given below.

Safety Devices
By paying strict attention to the recommended charging rates, it is possible to ensure that cell damage does not occur, due to the principle of cell balance developed by VARTA and incorporating charge reserve, discharge reserve and the antipolar mass. VARTA cells are protected against malfunction during charging and overcharging, and polarity reversal, within defined limits.

On the other hand, because the cell is only part of a complex system with numerous weak links, and because, in practice, it is often ill treated, intentionally or unintentionally, most of the VARTA series of sealed cells are fitted with safety vents. These prevent damage by misuse.

1. Button cells are not fitted with safety vents. They possess an inherent cell balance and are, moreover, operated under relatively low charge and discharge conditions. Due to their design, they can withstand a pressure of 75 bar, which is far beyond the normal equilibrium pressures found in button cells. Severe cases of mishandling of button cells lead to a rupture of the plastic sealing ring and, therefore, to cell failure.

2. Rectangular cells are provided with safety valves made in the form of plastic membranes. Because of their unsupported side area, they are more prone to mechanical deformation. The safety valves will operate at an internal pressure of 4—6 bar. After blowing, the cell continues to work like an open cell. It quickly loses capacity through increasing loss of electrolyte by evaporation and finally fails (section 4.4).

3. All types of cylindrical cells have resealing safety vents. Because of their mechanical strength, the safety vents operate at an internal pressure of 15—20 bar. After the vent has operated, the cell continues to work as a sealed system. As a result of the escape of gas, there is however an inevitable loss of cell balance. Eventual deterioration in performance and/or increasing loss of capacity will follow.

Table 5/1:
Common Misuse of Cells and the Consequences

Misuse	Consequence
Charging at an unnecessary high rate.	Uncontrolled overcharging, limits of charging voltage exceeded, excessive rise in pressure, leading to evolution of hydrogen, mechanical deformation of the case, damage to connectors, blowing of safety vents, permanent damage.
Charging at rated current at very low temperatures.	Recommended charging voltage exceeded, evolution of hydrogen, pressure build-up, consequences as above, permanent damage.
Charging at rated current at very high temperatures.	Restricted charging voltage, loss of charging efficiency, complete charge not possible, reduced extractable capacity, generally only a temporary phenomenon.
Storage at extremely high temperatures > 50 °C.	High self-discharge, low or no extractable capacity, ageing of the active mass in electrodes because of recrystallization, hydrolysis, and oxidation of separator and conductive material, carbonate formation in the electrolyte, mostly a temporary phenomenon, permanent damage when the period is of the order of months.
Polarity reversal	With button cells and at relatively low rates prolonged reversal possible. With sintered cells only permissible for short periods and at low rates, otherwise danger of hydrogen formation and pressure build-up. In consequence of the above permanent damage is possible.

5.2.6 Charging Efficiency, Charge Acceptance at High and Low Temperatures

5.2.6.1 Charging Efficiency

During the charging of a sealed cell, the electrical energy is stored as chemical energy. In general, it is not possible to recover the total energy added to the cell when it is subsequently discharged. The extractable energy is dependent on the charge acceptance under the operate conditions concerned.

The relationship between the effective and stored capacity is known as the charging efficiency, or Ah-efficiency, and is defined as:

$$\eta_{Ah} = \frac{\text{capacity available in Ah}}{\text{charge input in Ah}} \qquad [5/9]$$

Charging efficiency is dependent on cell type (cells with mass plate or sintered electrodes) and on the charging conditions, especially on the value of the charging current and the cell temperature.

When the rated current is used for complete charge and discharge at an average temperature of 20 °C, the ampere-hour efficiency is as follows:

for sealed cells with mass plate electrodes

$$\eta_{Ah} = 0.72,$$

for sealed sintered cells

$$\eta_{Ah} = 0.83$$

This signifies that with button cells approximately 72% and with cylindrical and rectangular sintered cells approximately 85% of the total capacity added can be returned as useful capacity.

The reciprocal of the Ah-efficiency is called the charge factor f_c:

$$f_c = \frac{1}{\eta_{Ah}} = \frac{\text{charge input in Ah}}{\text{available capacity in Ah}} \qquad [5/10]$$

For button cells this has a value of 1.4, for sealed sintered cells 1.2. Hence, 40% and 20% respectively are the amounts of extra capacity which have to be charged to replace the capacity previously discharged.

The "watt-hour efficiency" or "Wh-efficiency" is much less than the charging or Ah-efficiency. This is defined as the ratio between the available energy on discharge and the total energy input during charge:

$$\eta_{Wh} = \frac{\text{energy available in Wh}}{\text{energy input in Wh}} = \eta_{Ah} \cdot \frac{\text{mean discharge voltage}}{\text{mean charge voltage}} \qquad [5/11]$$

This ratio is smaller than the corresponding Ah-efficiency in comparison to the ratio between mean voltages during discharge and charge. For (full) charging and discharging at the nominal current at room temperature, it is calculated to equal:

for sealed cells with mass plate electrodes $\quad \eta_{Wh} = $ ca. 0.6
for sealed cells with sintered electrodes $\quad\quad \eta_{Wh} = $ ca. 0.73

This signifies that depending on cell type only about 60% and 73% respectively of the energy supplied during charge can be recovered on discharge. In practice, often a uniform charge factor is used. What is the reason for the discrepancy between the energy input during charge and that available on discharge? Section 5.2.2 included a detailed account of the side reactions which occur during charge and which are dependent on cell and ambient parameters. In fact, it is the evolution of oxygen which causes the discrepancy, and this occurs particularly near the end of the charging process, causing the charge factor to vary from the value one. The equilibrium potential, which is linked with the evolution of oxygen, does, in fact, have a higher value than the
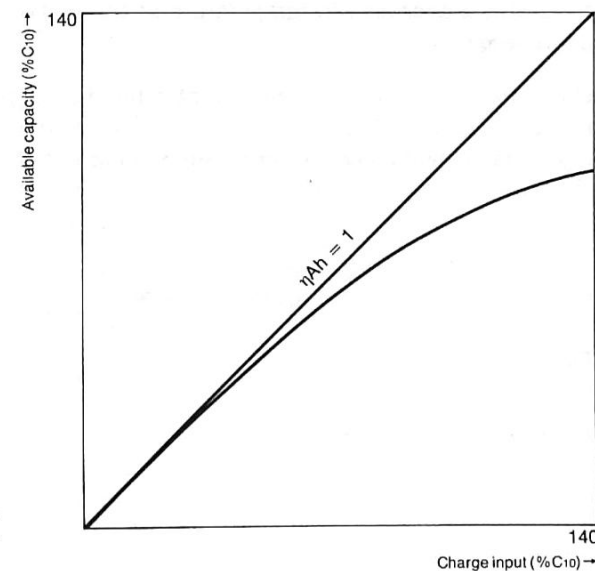
Fig. 5/19:
Ah-efficiency characteristic (ratio of available capacity to the charge input)

oxidation potential Ni^{2+}/Ni^{3+}. During the charging cycle the electrode polarization is greatly increased, and evolution of oxygen occurs, particularly towards the end of the charge.

There comes a point, as Fig. 5/19 shows, where there is a divergence from the 100% charging efficiency. Only at the start of charge is practically the whole of the added energy recoverable (shallow charge and discharge). Oxygen formation and pressure build-up and generation of heat are still absent here. During the charge cycle, the side reaction comes into play and the charging efficiency deteriorates.

5.2.6.2 Charge Acceptance at High and Low Temperatures

Fig. 5/20 gives the charging voltage characteristic of button cells with mass plate electrodes, type DKZ, and cylindrical sintered cells, type RS, for the 10-hour rate as a function of temperature. The charging voltage can be seen to rise sharply over the low temperature region, whilst it falls off quickly at high temperatures. The temperature coefficients recorded for sealed cells depend on the type of cell and the value of the charging current. The gradients generally lie between — 2mV/°C and — 4mV/°C.

Due to the high level of voltage, the charge acceptance of sealed cells at low temperatures is excellent. Because of the stabilizing control of higher nickel hydroxide at low temperatures, the side reaction of oxygen evolution is increasingly inhibited, and the charging efficiency rises.

On the other hand, the rate of gas recombination at the negative electrode falls with a decrease in temperature at the end-of-charge region, or during overcharge.

Under these conditions, there can be a build up of pressure, and due to high charging voltage, irreversible evolution of hydrogen occurs assuming that charging currents have not been adjusted to suit the ambient temperature.

Fig. 5/20:
End-of-charge voltage as a function of temperature for button cells type DKZ and cylindrical sintered cells type RS at charging current 0.1CA
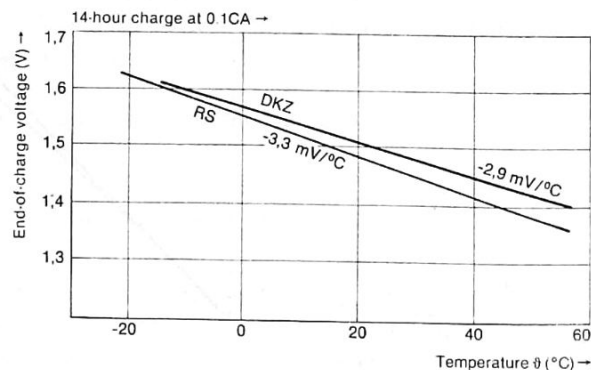
As a consequence, there is a risk that the cell may vent.

It is, therefore, imperative to prevent a charging voltage of more than 1.55V, or in special circumstances, 1.6V. This can be achieved by limiting the charge voltage to the specified cut off voltage, or at temperatures below 0 °C drastically reducing the rate of the charge current. In these circumstances, a correspondingly longer time is required to fully charge the battery.

It is found that only cells with sintered electrodes are really suited to low temperature charging. Even so, when temperatures fall below 0 °C, it is necessary to reduce the charging current if irreversible evolution of hydrogen is to be avoided (Fig. 5/21).

Fig. 5/21:
Recommended charge/ overcharge currents as a function of temperature
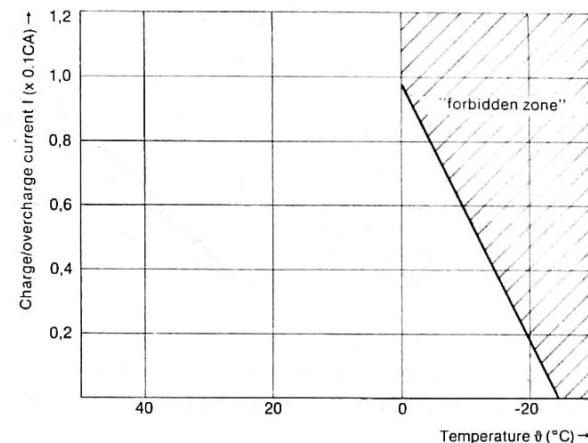
Hence, there are three necessary conditions for low temperature charging:

— reduced charge current with corresponding increase in charge time
— limiting of the charging voltage to a maximum of 1.6V, or preferably 1.55V
— provision of a resealing safety valve.

It is to ensure that high charge rates (accelerated charge, fast charge) should not be employed at low temperatures. It is, at least, necessary to comply with the recommended cut-off voltage.

Whilst the charge acceptance of sealed cells at low temperatures is very good because of the high voltage level characteristic, the charging efficiency falls rapidly at high ambient temperatures. For example, at 45 °C, which is the upper temperature limit for charging recommended by most manufacturers, the useful capacity stored is only 60—70% of the capacity supplied when charging at the nominal current. Even after prolonged overcharge, only a small increase in the extractable capacity is achieved. The cause of this

effect is directly connected with the lower charging voltage at higher temperatures (Fig. 5/20).

With charging voltages of about 1.4V, the necessary oxidation potential of the positive active mass is not reached, and the result is a deficit of highly oxidized nickel hydroxide in the positive electrode. Moreover, with increasing temperature there is also an increase in the side reaction which produces oxygen.

The reduced charge acceptance at high temperatures is shown in Fig. 5/22.
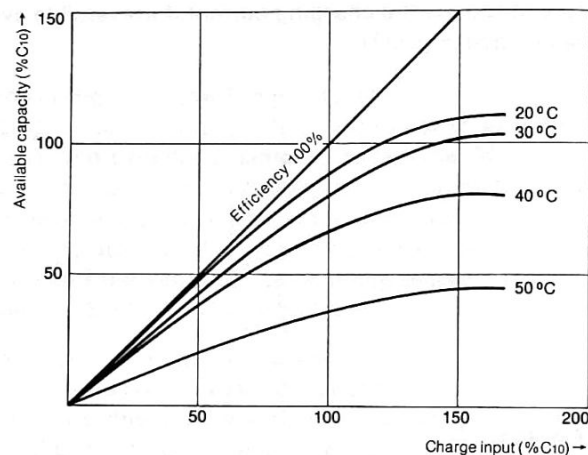
Fig. 5/22:
Available capacity as a function of charge input for cylindrical sintered cells type RS at various temperatures (charge 0.1CA, discharge 0.2CA at the same temperature)

Sealed cylindrical sintered cells type RS were charged at the nominal rate 0.1 CA and discharged at the same temperature at 0.2CA.
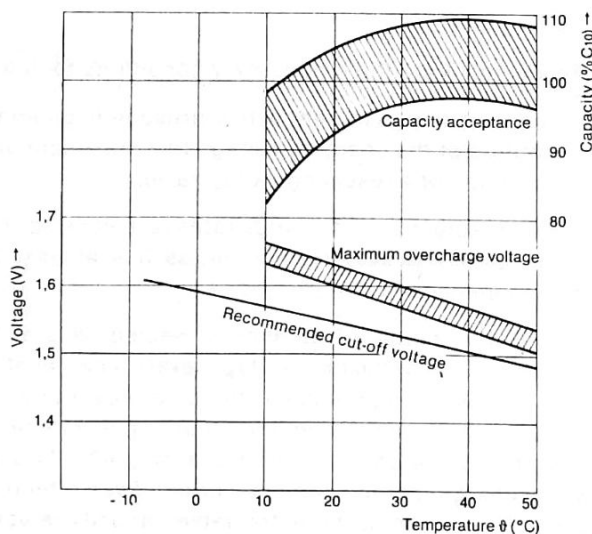
Fig. 5/23:
Recommended charging cut-off voltage, maximum overcharge voltage range, and range of capacity acceptance as a function of charging temperature for sealed rectangular sintered cells type SD fast charge at 1CA

In general, a better charge acceptance at high ambient temperatures can only be achieved when the charging voltage is raised by increasing the charging current correspondingly. Under these ambient conditions, fast charging therefore achieves a better charging efficiency than the use of normal charging currents.

For example, with sintered cells, as Fig. 5/23 shows, after charging at 10 x the nominal rate (1CA), almost all the extractable capacity realizable at room temperatures can be returned.

The limits that must be maintained when charging sealed cells can be derived directly from the relationships described. The critical values are given in Tables 5/2 and 5/3 below.

Table 5/2:
Charging current limits at room temperature (20 °C)

Series	Highest permitted charging current	Conditions/recommendations
Cells with mass plate electrodes		
Button cells DK	0.3CA	Voltage limit 1.49 V/cell (+ 0.01 V)
Button cells DKZ	0.3CA	Voltage limit 1.45 V/cell (+ 0.01 V)
Cells with combinations of sintered and pressed electrodes		
Cylindrical cells RSP	0.2CA	Voltage and/or time limited
Sintered electrode cells		
Cylindrical cells RS	2CA	Voltage and/or time limited
Special series RSH	2CA	Voltage and/or time limited
Special series RSX	2CA	Unregulated charge allowed
Rectangular cells SD	1CA	Voltage and/or time limited
Monoblock batteries 5 M	0.1 CA	—

In general:

— Button cells can be charged only at the rated current over the whole permitted temperature range. They are not rechargeable below 0 °C.

— The charging efficiency decreases at temperatures above 30 °C for all types of cell.

— With sintered electrode cells, (RS, SD) the charging currents suitable for the temperature conditions are:

above	30 °C	recommended current	0.2 CA
to	0 °C	recommended current	0.1 CA
to	− 10 °C	recommended current	0.05 CA
to	− 20 °C	recommended current	0.03 CA to 0.02 CA

More details are listed in Tables 9/2 and 9/6.

Table 5/3:
Charging temperature limits in °C

Series	Minimum temperature	Maximum temperature
Mass plate cells		
Button cells DK	0	45
Button cells DKZ	0	45
Cells with combinations of sintered and pressed electrodes		
Cylindrical cells RSP	0	50
Cells with sintered electrodes		
Cylindrical cells RS	−20	50
Special series RSH	−20	50
Special series RSX	−20	50
Rectangular cells SD	−20	50
Monoblock batteries 5 M	−20	50

5.3 Internal Resistance of Sealed Cells

5.3.1 D.C. Resistance
The variation in the terminal voltage of a cell from the off-load to on-load voltage is known as cell polarization or voltage drop. Its value and hence the voltage level during discharge is determined for a given constant current by the "internal resistance" of the cell. The internal resistance is made up of several components:

$$R_j \quad = \quad R_\Omega \quad + \quad R_c \quad + \quad R_r$$

Internal resistance   ohmic resistance   concentration resistance   reaction resistance

The ohmic component consists of resistive elements such as the current collecting leads, resistive parts of the electrodes (pockets, nickel wire grids, sintered grid and matrix material) and contact resistance at terminals. The ohmic component has a positive temperature coefficient. In order to achieve minimum internal voltage drop on load, it is necessary to minimize this resistive component by the choice of suitable materials with low specific resistance and the use of high cross-sectional areas and the shortest possible current paths. The on-load behaviour is, therefore, determined to a large extent by the cell type and its construction.

Sintered electrode cells have a much lower internal resistance, due to a higher metallic content in the sintered grid relative to the active mass than cells with mass plate electrodes, in which the active mass is pressed into retaining pockets made of nickel-plated sheet steel or into nickel wire grids. Sintered cells are, therefore, especially suited for applications where high discharge rates are involved and a good voltage characteristic is required.

The low internal resistance of sintered cells permits the use of batteries of lower nominal capacity than with mass plate cells for high rate discharge.

The resistance of the electrolyte is also associated with the ohmic resistance, but has a negative temperature coefficient, and a component which includes the resistive effect of the surface of the separator. The specific gravity of the electrolyte should be chosen for maximum conductivity. The choice of a suitable separator is of great importance. On one hand, it must allow unimpeded flow of electrolyte through the pores, on the other hand, there must be effective separation of the positive and negative electrodes. The polyamide mesh and grids used today largely fulfil these criteria. They are available in a width which allows them to be quickly made up into separators for specific applications.

The purely ohmic components of the internal resistance cause a linear increase in the internal voltage drop with increasing load current.

The current flow involves a transport of ions through the electrolyte. Thus the OH⁻ ions formed during discharge as reaction products at the nickel hydroxide electrode are transported into the electrolyte and thence towards cadmium electrode. This transport brings about a variation in the electrolyte concentration when the load is applied compared with the off-load condition, as seen between the pores in the electrodes and the bulk of the electrolyte. With increased current density, there is an increase of diffusion inhibition and this results in a decrease of the concentration of the reactants in the pores of the electrodes. Cell polarization then reaches a maximum when the electrolyte concentration at the electrode surface approaches zero. When this happens, there can be no further increase in load current. The concentration resistance component causes a non-linear rise in the cell polarisation up to a certain limit. For high currents, the capacity and voltage level are, therefore, not primarily determined by the amount and specific capacity of the active mass, but by the concentration and amount of the electrolyte ions bound and reacting in the electrode pores.

In order to keep this part of the internal resistance as low as possible, care must be taken to provide sufficient electrolyte at the electrodes for the expected loads. This is achieved by the use of large electrode surface area.

The aim here is to use the largest number of the thinnest possible electrodes. By raising the surface area, the current density for the required load current falls. It is possible to achieve a very high inherent porosity in electrodes and this is the best way of combating electrolyte deficiency at high loads. VARTA has, therefore, developed a series of special cells to meet all these demands.

The electrode mechanism consists of chemical reactions taking place in the pores of the electrode. The discharge reaction is accompanied by considerable changes: there are volumetric changes which alter the conductivity of the active mass, active centres are increasingly surrounded by the products of the discharge reaction, contacts within the carrier grid interrupted. All this means that during the course of a discharge, depending on the rate of discharge, the discharge processes become increasingly inhibited, a condition which causes additional polarization.

The D.C. resistance of a battery cell is determined by measuring the terminal voltages at various loads. If, for example, the terminal voltage (V_1) is measured after about 5 seconds on load at 0.2 CA (I_1), and again at a load of 2.2CA (I_2), then the current and voltage differences give the D.C. resistance as follows:

$$Ri = \frac{V_1 - V_2}{I_2 - I_1} = \frac{\triangle V}{\triangle I}$$

[5/13]

The D.C. resistance is dependent on the type of cell construction and its size (capacity), and on the actual conditions within the cell, state of charge and temperature.

Table 5/4 below gives an indication of the values for the D.C. resistance of sealed cells in the fully charged state at room temperature.

Table 5/4:
D.C. resistance (Ri) of sealed cells at 20 °C (approximate values).
Cell Condition: Fully Charged
Tolerance Limits Ri Approx. ± 20%

Cell Type	Ri (mOhm)	Cell Type	Ri (mOhm)
1. Mass Plate Button Cells		3. Rectangular Sintered Cells (SD)	
10 DK	4800	SD 1.6	16.0
20 DK	2200	SD 2.6	13.0
60 DK	1300	SD 7	8.0
100 DKO	500	SD 15	2.5
170 DK	375		
250 DK	300		
280 DK	200		
400 DK	170		
600 DK	190		
1000 DK	100		
225 DKZ	190		
600 DKZ	90		
1000 DKZ	50		
2. Cylindrical Sintered Cells, RS, RSH, RSX		4. Rectangular Monoblock Batteries	
		5 M 3	125
100 RS	140	5 M 6	101
180 RS	80		
225 RS	82		
452 RS	50		
500/501 RS	35		
RS 1	26		
RS 2	17		
750 RSH	20		
RSH 1.2	15		
RSH 1.8	12		
RSH 4	6.5		
RSH 7	5		
RSX 1	17		

Due to the fact that the structural parameters off sealed cells have a significant effect, more than for open cells, the relationship is not linear between internal resistance and cell capacity.

As already mentioned, far-reaching changes take place during the discharge reaction. In particular, the conductivity properties within the active mass vary widely. The inherently low initial internal resistance increases as the end of the discharge approaches. Fig. 5/24 shows the relative increase in resistance for sealed mass plate and sintered cells.

As was described in detail in section 5.4.8, the useful capacity and the voltage stability falls sharply during discharge at low temperatures. This phenomenon is primarily attributed to a dramatic rise of the internal resistance (Fig. 5/25). The diffusion process is increasingly inhibited by the drop in electrolyte conductivity at low temperatures, the internal voltage drop increases and the extractable capacity falls.
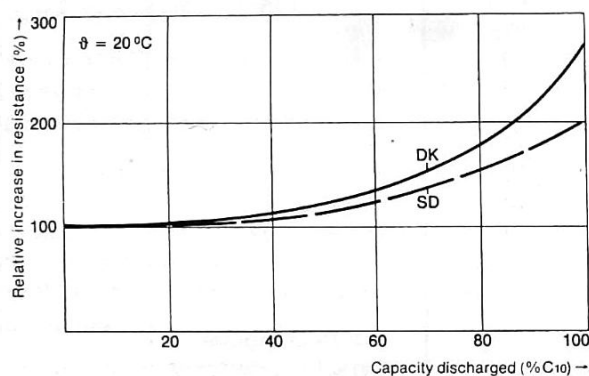
Fig. 5/24:
Relative increase in resistance as a function of the discharged capacity during discharge of mass plate button cells in the DK series, and rectangular sintered cell series SD, at room temperature
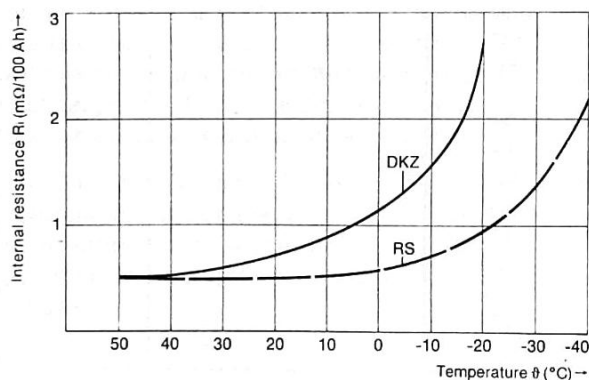
Fig. 5/25:
Internal resistance as a function of temperature for mass plate button cells in the KZ series and cylindrical sintered cells series RS based on 100 Ah nominal capacity

5.3.2 A.C. Resistance

Information on the A.C. resistance is of interest in many applications of sealed nickel cadmium batteries. For alternating voltages, the concentration changes in the electrolyte at the electrode surface show rapid variations which propagate as waves into the body of the electrolyte.

As will the D.C. internal resistance, it is not linear relationship compared with the rated capacity. The values of the A.C. resistance, therefore, depend on cell type and state of charge. With mass plate cells (button cells DK and DKZ), the values fall as the frequency rises. With sintered electrode cells (RS and SD cells), on the other hand, resistance rises in the high frequency range (10,000 Hz).

Table 5/5:
A.C. Resistances of Sealed Cells at 1,000 Hz
Cell State: Fully Charged
Ambient Temperature: 20 °C
Tolerance Limit R: Approx. ± 20%

Cell Type	R (mOhm)	Cell Type	R (mOhm)
1. Mass Plate		452 RS	
Button Cells		500/501 RS	
10 DK		RS 1	
20 DK		RS 2	
60 DK		750 RSH	
100 DKO		RSH 1.2	
170 DK		RSH 1.8	
250 DK		RSH 4	
280 DK		RSH 7	
400 DK		RSX 1	
600 DK			
1000 DK		3. Rectangular	
225 DKZ		Sintered	
600 DKZ		Cells SD	
1000 DKZ		SD 1.6	16
		SD 2.6	25
		SD 7	10
		SD 15	3.5
2. Cylindrical			
Sintered Cells,			
RS, RSH, RSX		4. Rectangular	
100 RS		Monoblock Batteries	
180 RS		5 M 3	101
225 RS		5 M 6	82

5.4 Capacity and Voltage Characteristics of Sealed Cells

The extractable capacity of a sealed cell depends on the rate of the discharge, the ambient temperature and on the final voltage as specified for the end-of-discharge. The voltage stability itself is likewise a function of load and temperature. A drop below the rated discharge current (0.1CA for cells with mass plate electrodes, or 0.2CA for sintered cells) gives no significant gain in capacity. An increase of the discharge current will result in a capacity drop which varies from type to type.

The following graphs give the values of discharge current in multiples of the nominal current 0.1CA (e.g. 0.1CA, 0.2CA, 1CA, etc.), whilst the capacity data refer to the nominal capacity at 0.1CA.

The graphs of the various discharge voltages also give the specified final voltages for the various loads, recommended by VARTA.

5.4.1 Capacity and Voltage Characteristics of DK Series Cells

Cells with mass plate electrodes for continuous loads up to $2C_{10}A$.
Capacity range: 10mAh to 1Ah.

Fig. 5/26:
Voltage characteristics as a function of discharge current for DK series cells at $0.1C_{10}A$ (1), $0.2C_{10}A$ (2) and $0.3C_{10}A$ (3) room temperature

Fig. 5/27:
Voltage characteristics as a function of discharge current for DK series cells at $0.5C_{10}A$ (1) and $1C_{10}A$ (2), room temperature

Fig. 5/28:
Available capacity as % of nominal capacity (C_{10}) as a function of discharge current for DK series cells, room temperature
1 ≙ 20 DK, 100 DKO, 280 DK,
2 ≙ 170 DK, 250 DK, 400 DK, 600 DK
3 ≙ 60 DK, 1000 DK

Fig. 5/29:
Initial (I), average discharge voltages (A), recommended final (F), and permitted final voltages (F_1) as function of discharge current for DK series cells at room temperature

5.4.2 Capacity and Voltage Characteristics of DKZ Series Cells

Cells with interleaved mass plate electrodes for continuous rates up to $3C_5A$.
Capacity range: 160mAh to 1Ah.

Fig. 5/30:
Voltage characteristics as a function of discharge current for DKZ series cells at $0.1C_5A$ (1), $0.2C_5A$ (2), and $0.3C_5A$ (3), room temperature

Fig. 5/31:
Voltage characteristics as a function of discharge current for DKZ series cells at $0.5C_5A$ (1), $1C_5A$ (2), and $2C_5A$ (3), room temperature

Fig. 5/32:
Available capacity as % of nominal capacity (C) as a function of discharge current for DKZ series cells, room temperature

Fig. 5/33:
Initial (I), average discharge voltages (A), recommended final voltage (F), and permitted final voltages (F_1) as functions of discharge current for DKZ series cells at room temperature
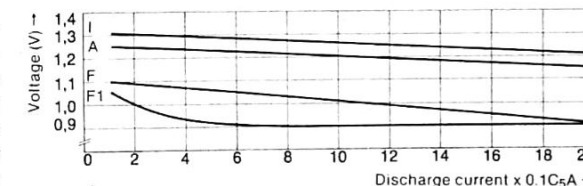
5.4.3 Capacity and Voltage Characteristics of RS Series Cells

Cells with coiled sintered electrodes in cylindrical cases can be continuously discharged up to $6C_5A$ (for RS cells $\leq$ 1Ah) respectively $4C_5A$ (for RS cells $\geq$ 1Ah).
Capacity range: 100mAh to 7Ah.

Note: Capacities and voltage characteristics of special cells for extremely high loads can be found in section 5.5.
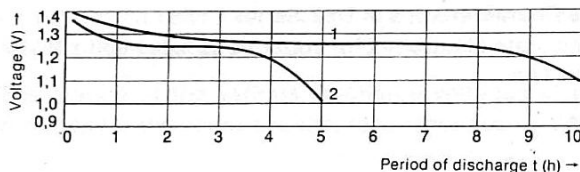
Fig. 5/34:
Voltage characteristics as a function of discharge current for RS series cells at $0.1C_5A$ (1) and $0.2C_5A$ (2) room temperature
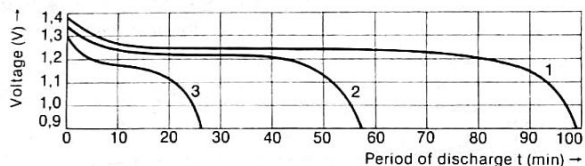
Fig. 5/35:
Voltage characteristics as a function of discharge current for RS series cells at $0.6C_5A$ (1), $1C_5A$ (2), and $2C_5A$ (3), at room temperature
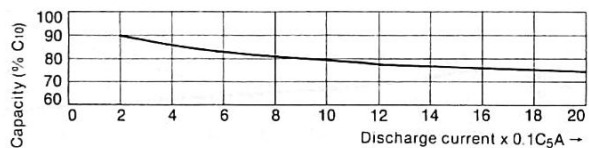
Fig. 5/36:
Available capacity as % of nominal capacity (C) as a function of discharge current for RS series cells at room temperature
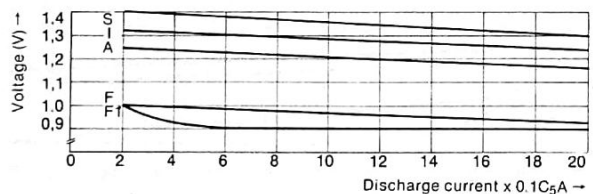
Fig. 5/37:
Starting (S), initial (I), average discharge voltages (A), recommended final voltages (F), and permitted final voltages (F_1) as functions of discharge current for RS series cells at room temperature

5.4.4 Capacity and Voltage Characteristics of RSP Series Cells

Cells with pressed sintered electrode combinations for continuous loads up to $10C_5A$.
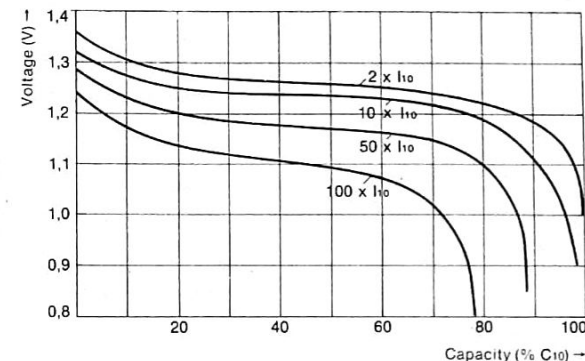
Fig. 5/38:
Discharge voltage characteristics as a function of available capacity as % of nominal capacity (C) for RSP series cells at different discharge currents at room temperature

Fig. 5/39:
Available capacity as % of nominal capacity (C) as a function of discharge current for RSP series cells at room temperature
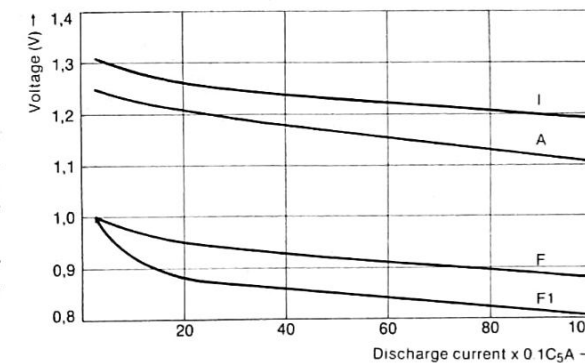
Fig. 5/40:
Initial (I), average discharge voltages (A), recommended final voltage (F) and permitted final voltages (F_1) as functions of discharge current for RSP series of cells at room temperature

5.4.5 Capacity and Voltage Characteristics of SD Series Cells

Cells with interleaved sintered electrodes for continuous loads up to $4C_5A$.
Capacity range: 2.4 to 15Ah.
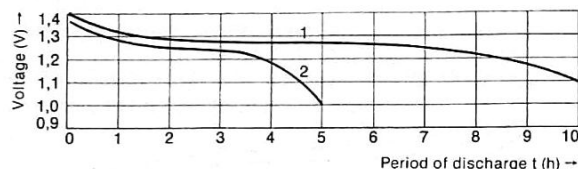
Fig. 5/41:
Voltage characteristics as a function of discharge current for SD series cells at $0.1C_5A$ (1) and $0.2C_5A$ (2), room temperature
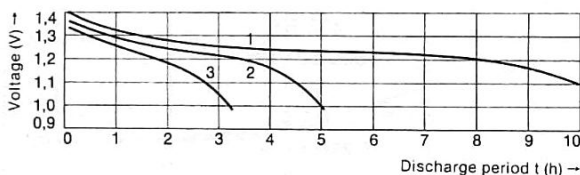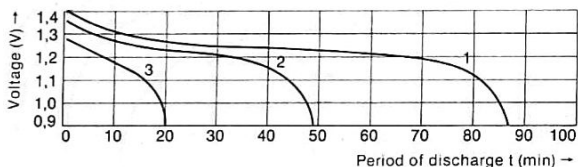

Fig. 5/42:
Voltage characteristics as a function of discharge current for SD series cells at $0.6C_5A$ (1), $1C_5A$ (2), and $2C_5A$ (3) room temperature

Fig. 5/43:
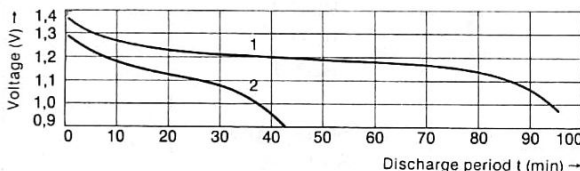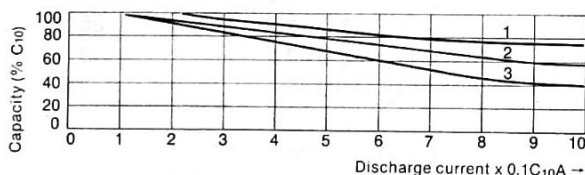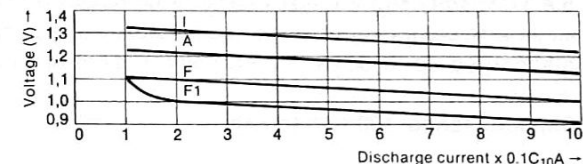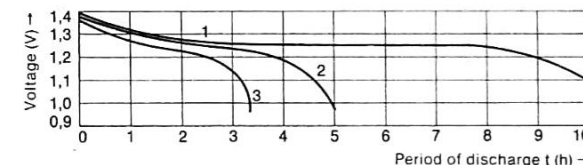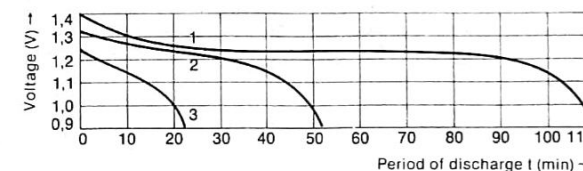*Available capacity as % of nominal capacity (C) as a function of discharge current for SD series cells at room temperature*
1 ≙ Cells SD 1.6 to SD 7
2 ≙ Cell SD 15

Fig. 5/44:
Starting (S), initial (I), average discharge voltages (A), recommended final voltage (F), and permitted final voltages (F_1) as functions of discharge current for SD series cells at room temperature

5.4.6 Capacity and Voltage Characteristics of 5 M Series Batteries

5-celled Monoblock batteries with interleaved sintered electrodes in plastic cases for continuous loads up to $1C_5A$.
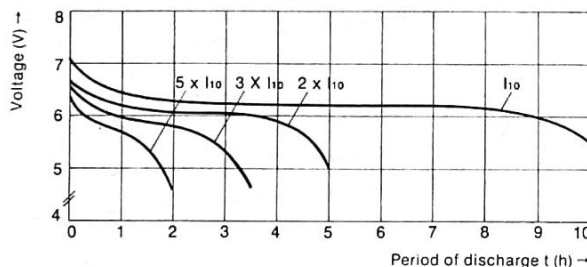
Fig. 5/45:
Voltage characteristic as a function of discharge current for 5 M series batteries at various loads at room temperature

Fig. 5/46:
Available capacity as % of nominal capacity (C) as a function of discharge current for 5 M series batteries at room temperature
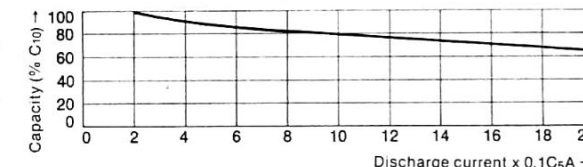

Fig. 5/47:
Initial (I), average discharge voltages (A), recommended final voltage (F), and final voltages (F_1) as functions of discharge currents for 5 M series batteries at room temperature
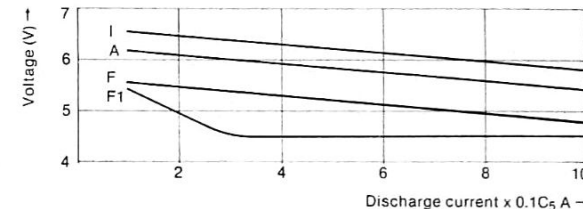
5.4.7 Efficiency and Energy Storage

The Ah- and Wh-efficiencies of sealed cells have been described in detail in section 5.2.6. They have been calculated from the charge factor of 1.4 for mass plate cells and 1.2 for sintered cells at the cell's rated charge and discharge rates at +20 °C.

The actual charging efficiency and energy content on the other hand are directly related to the available capacity, the charge and discharge currents and on the ambient temperature. Considering the capacity and voltage curves given in sections 5.4.1 to 5.4.6 the mean load data given in Table 5/6 have been obtained. These have been averaged over the whole range of cell types and represent a guide to minimum values of capacity. Except for the DK series, the results are based on the 5 hour discharge rate ($0.2C_5A$).

As already mentioned, the available energy is closely related to the rate of discharge and the temperature. Figs. 5/48 and 5/49 give details of the useful energy of sealed cylindrical sintered cells RS and mass plate button cells DKZ over the temperature range from —45 °C to +50 °C for loads between $0.1C_5A$ to $4C_5A$ for RS cells, and $2C_5A$ for DKZ cells. Cells were charged at the nominal rate at room temperature, then were allowed to stand for 6 hours to attain the ambient temperature.

Table 5/6:
Efficiency and energy content of sealed cells at room temperature (based on 5 hour rate)

	Effective Efficiency		Energy per Unit Volume	Energy per Unit Weight
	ηAh	ηWh	Approx. Wh/l	Approx. Wh/kg
Button cell DK	0.76	0.650	61**	21.0**
Button cell DKZ	0.76	0.655	62	22.0
Cylindrical Cell RS	0.85	0.760	78	27.0
Cylindrical Cell RSP	0.76	0.660	81	28.0
Special Series RSH	0.82	0.730	90*	28.5*
Special Series RSX	0.80	0.715	78*	23.7*
Rectangular Cell SD	0.79	0.700	52	21.0

* 1-hour discharge rate   ** 10-hour discharge rate

Fig. 5/48:
Available energy (%) as a function of temperature for cylindrical sintered cells types RS at various loads
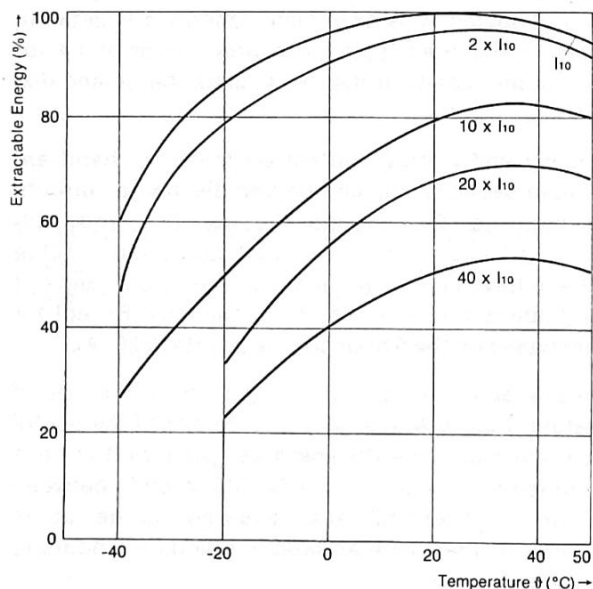
As can be seen, the useful energy decreases very quickly at low temperature for mass plate cells at relatively low discharge rates. Therefore, these cells are only recommended for use down to —20 °C.
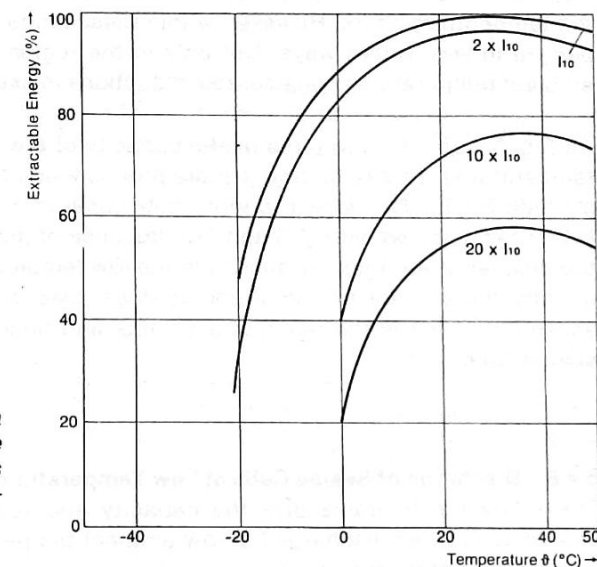
Fig. 5/49:
Available energy (%) as a function of temperature for mass plate button cells of the DKZ series at different discharge rates

5.4.8 Capacity as a Function of Temperature
The recommended working range and temperature limits vary widely from one manufacturer to another, and also whether charge, discharge, or storage of sealed cells is concerned.

The following temperature ranges apply to VARTA cells:

Table 5/7:
Limiting temperatures related to type of operation for sealed nickel cadmium batteries.
For operating conditions, refer to Table 9/2.

Type of Operation	Cells with Mass Plate Electrodes	Cells with Sintered Electrodes
Discharge	-20 ºC ÷ 60 ºC	-45 ºC ÷ 60 ºC
Charge	0 ºC ÷ 45 ºC	-20 ºC ÷ 50 ºC
Storage	- 40 ºC ÷ 60 ºC	-45 ºC ÷ 60 ºC

The temperature ranges refer to normal discharge rates. They are valid for discharge up to approximately the 1 hour rate (1CA), but apply to charging currents at the 10 hour rate (0.1CA).

The non-uniform working ranges indicate that different mechanisms control the temperature limits. However, within these limits the cells can be seen to behave in very varied ways. Not only in the region of high but also in low ambient temperatures considerable reductions in useful capacity is noticed.

As Fig. 5/9 above shows, the useful capacity of the cells falls rapidly at low temperatures. This reduction is more pronounced at high rates of discharge (section 5.1.2.). This effect is more noticeable in mass plate cells (DK and DKZ) than sintered cells (RS and SD). Because of increased cell polarization the discharge voltages fall sharply in the low temperature region, and consequently the amount of useful energy (Figs. 5/48, 5/49). In conclusion, it is essential to define the temperature limits and hence the working range of sealed cells.

5.4.8.1 Discharge of Sealed Cells at Low Temperatures
The following diagrams give the capacity and voltage characteristics of sealed cells when discharged at low ambient temperatures. Charging at the nominal rate at room temperature (20 °C).
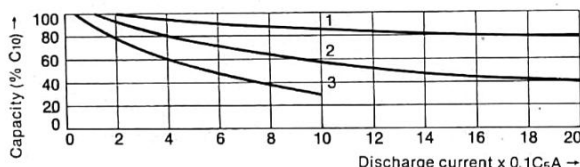
Fig. 5/50:
Available capacity as % of nominal capacity (C) as a function of discharge current for DKZ series cells at 20 °C (1), 0 °C (2), and —20 °C (3)
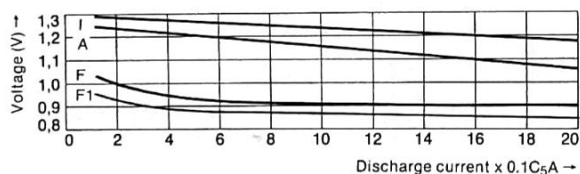
Fig. 5/51:
Initial (I), average (A) discharge voltages, recommended (F) and permitted final voltages (F₁) as functions of discharge current for DKZ cells at 0 °C
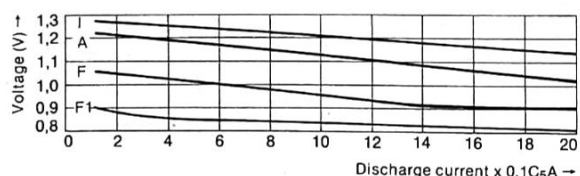
Fig. 5/52:
Initial (I), average (A) discharge voltages, recommended (F) and permitted final voltages (F₁) as functions of discharge current for DKZ cells at —20 °C
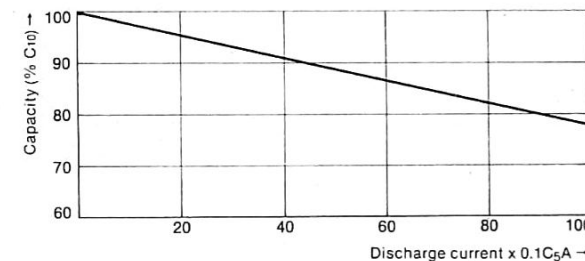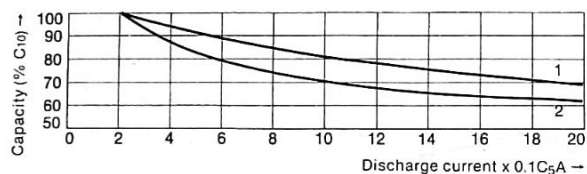
Fig. 5/53:
Available capacity as % of nominal capacity (C) as function of discharge current for SD series cells (up to 10Ah) at temperatures of 0 °C (1) and —20 °C (2)
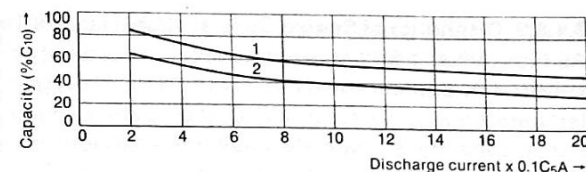
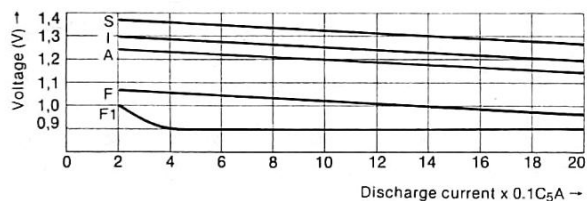**Fig. 5/54:**
Starting (S), initial (I), average discharge voltages (A), recommended (F) and permitted final voltages (F₁) as functions of discharge current for SD type cells (up to 10Ah) at 0 °C
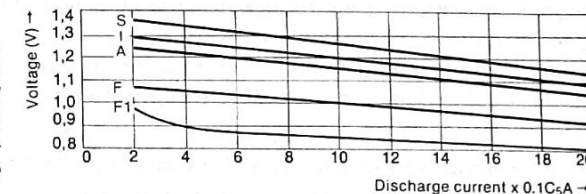
Fig. 5/55:
Starting (S), initial (I), average discharge voltages (A), recommended (F) and permitted final voltages (F₁) as functions of discharge current for SD type cells (up to 10Ah) at —20 °C
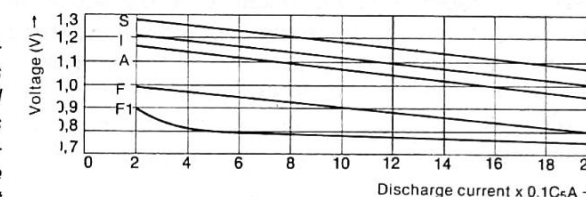
Fig. 5/56:
Available capacity as % of nominal capacity (C) as a function of discharge current for RS type cells (e.g. RS 2) at 0 °C (1), and —20 °C
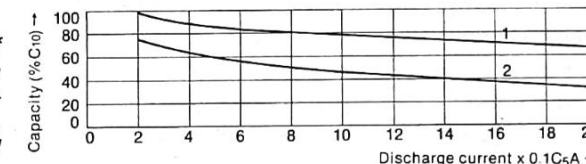
Fig. 5/57:
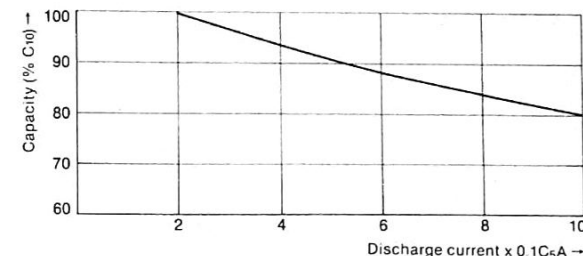*Starting (S), initial (I), average discharge voltages (A), recommended (F) and permitted final voltages (F₁) as functions of discharge current for RS type cells (e.g. RS 2) at 0 °C*
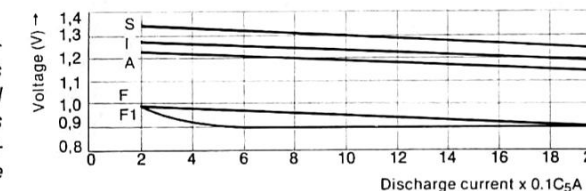
Fig. 5/58:
Starting (S), initial (I), average discharge voltages (A, recommended (F) and permitted final voltages (F₁) as functions of discharge current for RS type cells (e.g. RS 2) at —20 °C
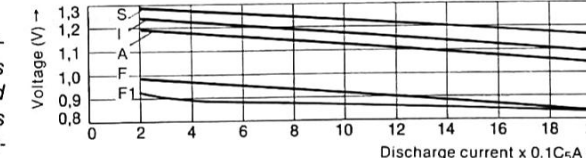
5.4.8.2. Discharge of Sealed Cells at High Ambient Temperatures

As Figs. 5/9 and 5/10 show, the maximum capacity occurs at an ambient temperature of approximately 27 °C to 30 °C. At higher temperatures including temperatures up to about 45 °C, the useful capacity is reduced. This reduction in capacity is relatively small if the previous charge cycle of the cell took place at normal ambient temperature. It is generally caused by storage at high temperature prior to the discharge, when there is a distinct partial decomposition of the higher nickel hydroxides of the active mass, which depends on the temperature and duration of the storage. The effect is relatively small and the topic will not be illustrated further.

5.4.8.3 Charge and Discharge at Low and High Temperatures

This discussion refers to discharge at low or high temperatures following a charge at room temperature (20 °C) and a subsequent storage period at the discharge temperature. In many practical applications however, charge and discharge are carried out at the same temperature (cycling at ambient conditions). Thus the amount of cell polarization occurring at the high temperatures during discharge is also affected by the changed efficiencies resulting from charging at other than room temperature (section 5.2.6).

The construction of satisfactory generalized characteristics encompassing the behaviour of a whole series of cells is not realistic, because the type of construction, cell geometry, charging current and charge factor, storage time and discharge current have highly complex relationships. As an example, RS cells will now be considered with respect to some standard operating conditions.
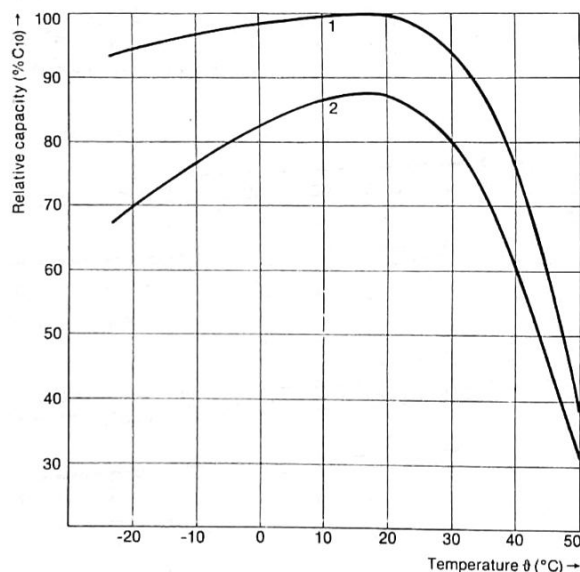
Fig. 5/59:
Available capacity as a % related to the nominal capacity (C) as a function of temperature for discharge currents of $0.2C_5A$ (1) and $1C_5A$ (2) for RS type cells following a charge at 0.1CA charge factor 1.4, and rest time 1 h

The following parameters were selected in the presentation of Fig. 5/59 to record the results of a series of tests: temperature changes during charge and discharge, charging currents and charge factors, shelf times and discharge currents.

Temperature Range: —20 °C to + 50 °C
Storage Time: 1 hour
Charging Current: 0.1CA
Discharge Current: 0.2CA and 1CA
Charging Factor: 1.4

It can be seen from the curve that during cyclic operation, i.e. charge and discharge, at temperatures above 35°C, in contrast to the results shown in Fig. 5/9, the useful capacity declines sharply when charged at nominal current and normal charge factor. To obtain better results, it is necessary to overcharge at higher current or use a greater charge factor.

The drop in capacity observed in the high temperature region is much more marked than in the low temperature range. This fact is to be attributed directly to good charge acceptance at lower temperatures (section 5.2.6).

On the other hand, the statistical spread of capacity over this temperature range is particularly large. In addition, variation in the end-of-charge voltage is so wide that general use of the 0.1CA charging current appears inadvisable. Irreversible evolution of hydrogen must be expected in such cases (Figs. 5/20 and 5/21).

It is generally true that in sealed cells, especially at high rates the ambient temperatures are modified by the conditions within the cells. Thus the cell temperature rises rapidly during fast discharge at low temperatures, so that significantly more capacity can be extracted than under isothermal conditions. For the same amount of current the heating effect is greater, the greater the internal resistance of the cell. Quite an appreciable amount of heat is also generated during charge and overcharge as a result of exothermic gas recombination. The amount of heat superimposed on the ambient conditions is dependent on the type of cell and the current. The effects are so complex that no generalized characteristics can be given which are valid for all the types of cells. The examples quoted in the above section are, therefore, based on quasi-isothermal conditions.

5.5 Special Types for Extreme Operational Requirements
Standard cell types

— button cells with mass plate electrodes with simple or interleaved assembly (DK and DKZ respectively),
— rectangular cells with interleaved sintered electrodes (SD or 5 M in block form),

— cylindrical cells with coiled sintered electrodes (RS) or a combination of sintered and pressed electrodes (RSP),

are satisfactory for most users' requirements. With proved designs, they have over the years been continually adapted to meet the needs of the user. On the other hand, in recent years a great number of new fields of application have occurred, having requirements that the standard cell types cannot fully satisfy. Moreover, there are those applications which go far beyond the performance available from standard designs.

For example, there are very high discharge currents close to short-circuit conditions, an increase in upper and lower temperature ranges, prolonged storage under very severe ambient conditions, the fastest possible uncontrolled charge, and many other requirements.

At present, it is neither economical to try to make cells which simultaneously satisfy all these severe conditions, nor does it seem to be technically feasible. To adapt cells to these conditions requires the introduction of, or special emphasis on, structural parameters and production techniques. In fact, the most important parameters which affect the behaviour of cells, for example electrode thickness and porosity, charge reserve and discharge reserve, electrolyte quantity, density, and additions thereto, connecting leads, materials, and manufacturing methods must be carefully adjusted to the operational conditions.

Because many of the cell parameters mentioned above have inter-related effects and are often incompatible, it is, therefore, not possible to optimize the cells' design in the desired direction without adversely affecting other desirable parameters. Because certain applications are outside the normal range of requirements, VARTA has produced a series of special cells tailored to meet specific needs.

5.5.1 Cells for High Rate Discharge

A special series of cylindrical cells has been produced for very high rate discharge applications, having a very low internal resistance. They are known as the RSH series.

Fig. 5/60 shows the discharge voltage characteristic of a cell type RSH 1.2, compared with the same sized cells, standard RS 1.2, and having the same nominal capacity. The 200 mV higher working voltage and the greater useful capacity prove the superiority of this heavy duty type. At loads of 100 times the nominal current, the H-type cell returns more than double the energy of the standard type. At the 5-hour discharge rate, the Ah- and Wh-efficiencies are very similar to those of standard cells (Table 5/6).

Fig. 5/60:
Discharge voltage characteristic as a function of discharge duration for discharge rates of $8C_5A$ (1) and $10C_5A$ (2) for RS type cells (e.g. RS 1.2) and RSH (e.g. RSH 1.2) at room temperature
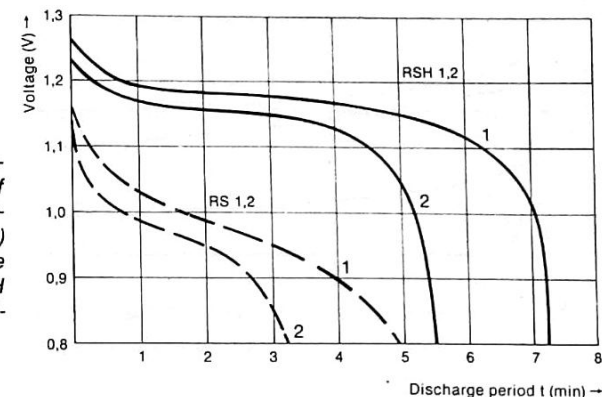
The following diagrams give the capacity and voltage characteristics of the series at discharge rates up to $10C_5A$ (Fig. 5/61 and 5/63).

Fig. 5/61:
Discharge voltage characteristic as a function of the available capacity in % of the nominal capacity (C) for RSH series cells at different discharge currents at room temperature
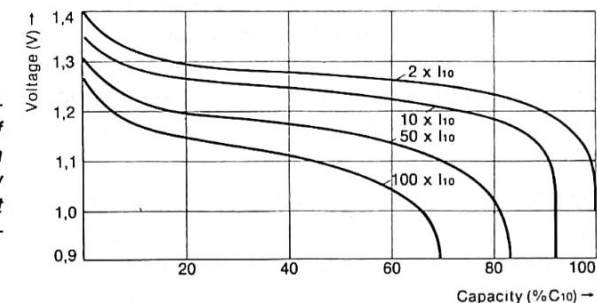
Fig. 5/62:
Available capacity as % of nominal capacity (C) as a function of the discharge current for RSH series cells at room temperature
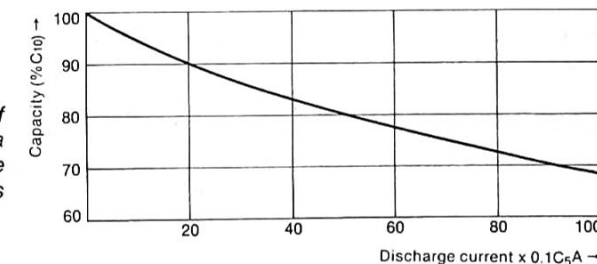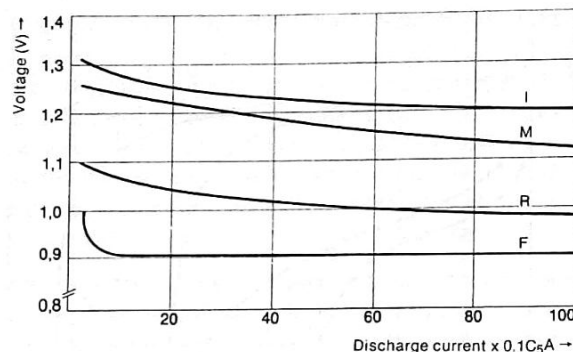
Fig. 5/63:
Initial (I), mean discharge voltages (M), recommended (R), and permitted final voltages (F) as functions of the discharge current for RSH series cells at room temperature

Voltage (V) axis; Discharge current x 0.1C$_5$A →

The discharge characteristics are comparable with those of the RSP series. The working range of RSH cells is however much wider, and they can be used at charge rates up to 1C$_5$A. The temperature range, down to —45 °C, is also significantly wider.

5.5.2 Cells for Very High Charge Rates

As was mentioned in section 5.2 with reference to the charging of sealed cells, certain limits must be set for current and temperature (Tables 5/2 and 5/3). There are however certain applications in which cells have to be fully charged within a very short period, and for various reasons no proper control of the charge, time or voltage is possible, so that increased cell temperatures occur.

VARTA has also developed a special series to meet these requirements, which are designated "RSX". They have a good capacity/volume ratio with special electrodes and carefully designed cell balance, which allow the unregulated use of charging currents of up to 2C$_5$A for extended periods. As the capacity and voltage characteristics given in Figs. 5/64, 5/65 and 5/66 show, these cells exhibit excellent discharge performance related to extractable capacity and voltage stability, which point to the outstanding characteristics of this series.

Fig. 5/67 gives the voltage and temperature characteristics on charge and overcharge for a cell type RSX 1 at rates up to 1.5C$_5$A. Comparison with Fig. 5/15 will show the superiority of this series regarding the charging characteristics. After charging to about 150% of the nominal capacity, voltage and temperature equilibrium is reached, and safe overcharge, even over an extended time, is possible without harmful side effects. The temperature coefficient of the end-of-charge voltage for these special types is about —1.63 mV/°C.
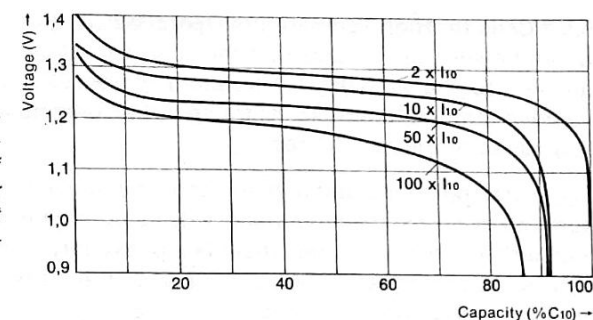
Fig. 5/64:
Discharge voltage characteristic as a function of extractable capacity as % of nominal capacity (C) for RSX series cells (RSX 1) at various discharge currents at room temperature

Voltage (V) axis; curves labelled 2 x I$_{10}$, 10 x I$_{10}$, 50 x I$_{10}$, 100 x I$_{10}$; Capacity (%C$_{10}$) →
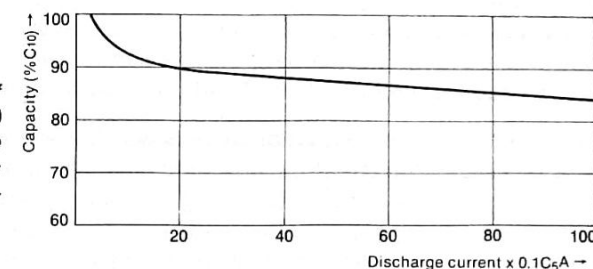
Fig. 5/65:
Available capacity as % of the nominal capacity (C) as a function of discharge current for RSX series cells (RSX 1) at room temperature

Capacity (%C$_{10}$) axis; Discharge current x 0.1C$_5$A →
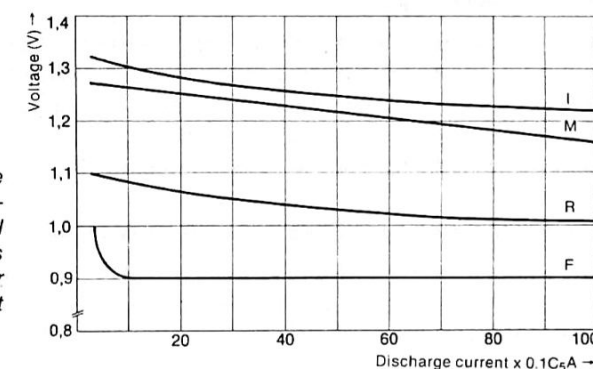
Fig. 5/66:
Initial (I), mean discharge voltages (M), recommended (R) and permitted final voltages (F) as functions of discharge current for RSX series cells (RSX 1) at room temperature

Voltage (V) axis; Discharge current x 0.1C$_5$A →
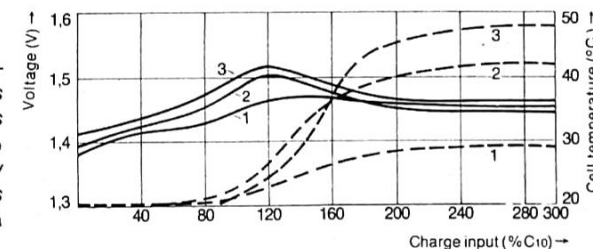
Fig. 5/67:
Charging voltage and temperature characteristics (broken lines) as functions of charge supplied as a % of the nominal capacity (C) for RSX series cells (RSX 1) at rates f 0.3C$_5$A (1), 1C$_5$A (2), and 1.5C$_5$A (3)

Voltage (V) axis; Cell temperature (°C) axis; Charge input (%C$_{10}$) →

5.5.3 Cells for High Temperature Operation

It can be seen in Fig. 5/22 that the charging efficiency of sealed cells drops quickly as the ambient temperature increases. At the maximum recommended temperature of 45 °C for charging, only about 60—70% of the nominal capacity will be returned.

In general, no permanent damage should occur with an occasional high temperature cycle. On the other hand, when sealed cells are used continuously in high ambient temperatures, there is a possibility of irreversible damage. Not only is the performance reduced but also the battery life. The cause of the problem is primarily attributed to the increase in the rates of certain chemical reactions taking place within the cell at these high temperatures. The most important are hydrolysis of the separator material coupled with a de-activating effect of the decomposition products, and in the case of mass plate cells powerfully accelerated oxidation of the conductive material (graphite) which, in turn, causes the formation of carbonate within the cell (section 5.6.3.2).

In the design and construction of cells which are designed for high temperature service, all the structural elements must, therefore, be made of materials that have a high resistance to ageing. Sealants, plastic inserts and the separator must also be able to withstand the temperature reached during service. Furthermore, those factors which lead to severe carbonate formation in mass plate cells must be kept to a minimum. The properties of the graphite used are of special importance here.

The charge acceptance of the electrodes themselves has been increased and this has significantly improved the charging efficiency. By the development of special electrodes and adding some stabilizing features, VARTA has succeeded in producing special cells which are able to cope with service temperatures up to 75 °C. They are designated as "RST" cells.

Cells in this series have the following advantages, among others:

— Chargeable at nominal charging currents at temperatures up to 75 °C.
— Charge acceptance at very high temperatures is about twice as much as for RSH cells.
— High extractable capacities at temperatures between 75 °C and —20 °C (almost comparable with RSH).
— Very good trickle charge characteristics: these cells can be overcharged for months at up to $0.1C_5A$.
— About 50% reduction in self-discharge through use of stabilized electrodes.

The voltage stability of this type of cell, specially developed for high temperature operation, is however not as good as that of RSH cells; also, they are less suitable for high rate discharge applications. For such purposes, therefore, the choice should be RSH or RSX cells.

5.6 Operational Behaviour of Sealed Cells

5.6.1 Types of Operation

Specification VDE 0510 differentiates between the following types of service:

Battery Operation

In this service, the load is supplied by the battery alone. It is thus a pure form of cycling. When the battery is discharged, it is disconnected from the load and put on charge, using a charging unit and taking into account the rated charging current and the charge factor for the specified conditions (Fig. 5/68).
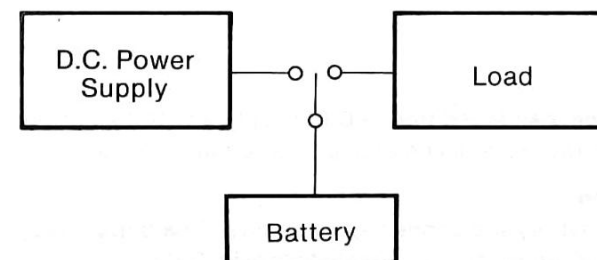
Fig. 5/68:
Block diagram of battery operation

Changeover Operation

Battery and the load are separate. While the load is being supplied from a D.C. mains source, the battery, separated from the load, is kept fully charged by a charger (see Trickle Charging). If the D.C. supply to the load should fail, then the battery is switched in, in order to maintain the supply (Fig. 5/69).
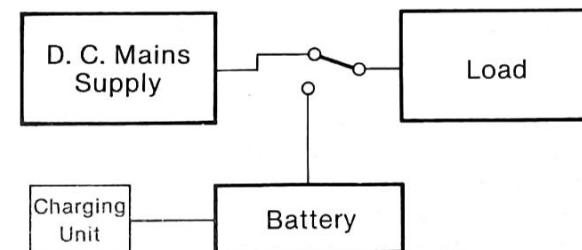
Fig. 5/69:
Block diagram of changeover operation

Standby Operation

In this type of service, the load and the battery are permanently connected in parallel. Both are permanently fed from the same D.C. supply (Fig. 5/70). Sintered cells are only suited to this type of service.
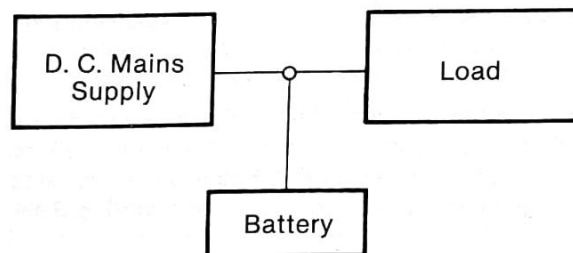
Fig. 5/70:
Block diagram of standby operation

Buffer Operation

For this type of service, the load is fed from a D.C. supply whilst the battery serves merely as a peak power source and acting as a voltage regulator.

Standby Parallel Operation

The D.C. supply and the battery are connected in parallel. The battery only supplies current to the load when the D.C. supply fails (Fig. 5/70).

For the types of operation described here, there are two basic types of load for which the battery is used, cycled operation, or trickle charge.

5.6.1.1 Cyclic Operation

Cyclic operation consists of a series of regularly repeated charge and discharge phases separated from each other. The current and periods involved must be chosen to match the operational requirements concerned.

The "service life" of the cell is defined as the number of cycles which the cell will provide before falling below a certain minimum useful capacity (as % of the nominal capacity) (section 5.6.3).

5.6.1.2 Trickle Charge Operation

For this type of load, the battery is not regularly discharged as in cycled operation. The main feature is that the battery is kept in the fully charged condition in order that it can supply the necessary current on demand. To that end, it is necessary to compensate for any loss of capacity through self-

discharge (section 5.6.2). This is done after the battery has first been fully charged by connecting it to a D.C. supply known as a trickle charger. For mass plate cells, this charging current is $0.01CA$ for sintered cells $0.02C_5A$ to $0.05C_5A$. The use of a voltage controlled trickle charge, as for open cells, is not possible with sealed cells.

5.6.1.3 Effective Service Life of Sealed Cells

There is a noticeable loss of capacity and ability to supply the rated current during the course of time, depending on the type of service and the rate of discharge applied to the cells. Thus, the extractable capacity falls steadily until it falls below a specified limit. Fig. 5/71 gives the capacity characteristic of a sealed rectangular sintered cell under cycled operation. The causes of this loss of capacity are discussed in section 5.6.3.

Fig. 5/71:
Effective capacity as % of the nominal capacity (C) as a function of number of cycles for SD series cells under cyclic conditions
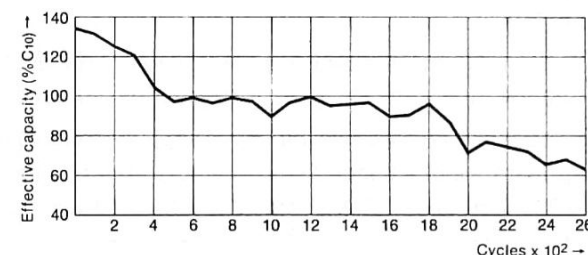
At this point, it is pertinent to refer to some phenomena which are observed during trickle charge. These include a temporary drop in voltage and capacity after trickle charging, also the possible occurrence of a "two-step" discharge characteristic.

During discharge of a battery after a long period of trickle charging, a discharge characteristic which is noticeably different from that of a freshly charged cell occurs. There is a marked drop in the average discharge voltage. This fall in voltage and hence a loss in capacity is related to length of the trickle charge period as well as on the rates used. With vented cells, which are given relatively low trickle charges of about $0.001CA$, or less, there is a much lower extractable capacity down to the specified final voltage than there is after a normal charge. In contrast, with sealed cells, which are maintenance free, comparatively high trickle charge currents of 0.01 to $0.05CA$ are used. After trickle charge service, these cells also show a marked drop in voltage, but there is no significant drop in capacity (Fig. 5/72).
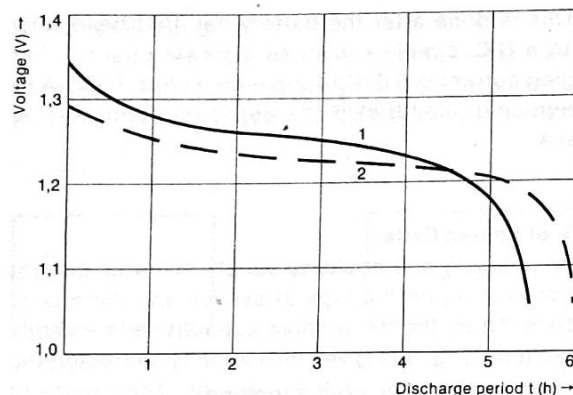
Fig. 5/72:
Discharge voltage characteristic as a function of discharge period for SD series cells at discharge current of $0.2C_5A$ after a normal charge (1), and after a 9 month trickle charge at $0.03C_5A$ (2)

The drop in voltage does, however, depend on the discharge current. Whereas at $0.2C_5A$, it is relatively low (20—25 mV), it can — depending on the charging time — at $1C_5A$ be as much as 50—80 mV. A drop in capacity can also be expected.

The cause of this effect is an increase in crystal size in the active mass during the trickle charge. It leads to additional polarization within the cell.

In sintered electrode cells, this effect is often subordinate to another, the appearance of a second step (memory effect) in the discharge characteristic. When cells which have been on a long charge are put on discharge, the characteristic exhibits a marked voltage step. The width of this second step is greater, the longer the charging period (Fig. 5/73).
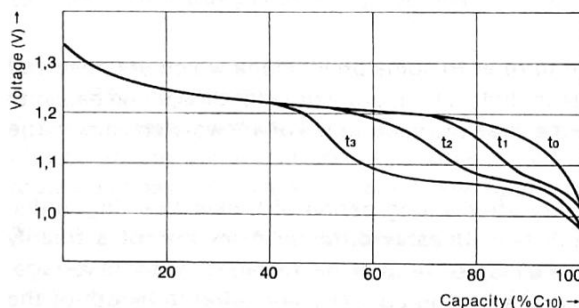
Fig. 5/73:
Discharge voltage characteristic as a function of the capacity delivered in % of nominal capacity (C) after different periods of trickle charging (growth of the second discharge step)

High temperatures also contribute significantly to this phenomenon. The same effect can also be observed when cells are only partly charged and discharged (shallow cycle). When the subsequent full discharge is attempted, only a part of the total capacity is returned for the usual voltage level. It appears as if the cell has "remembered" the partial discharge during the previous cycles, hence the term "memory effect". The appearance of the second

step in the discharge characteristic is, therefore, undesirable because, generally speaking, after trickle charging, up to 40% of the nominal capacity has been extracted, there will be a fall of about 80—120mV. Hence, if a high end-of-discharge voltage is required, the discharge is sometimes severely limited, i.e. the capacity is very much reduced.

There has been no shortage of attempts at an explanation. Intensive research has proved that the negative electrode alone is responsible for this effect. The cause was formerly attributed to progressive formation of carbonate in the electrolyte. This explanation was not really satisfactory, because the effect can be reversed by a brief period of cycling. Furthermore, a definite increase in crystal size was observed after prolonged use of low charging currents, and particularly at high temperatures. Active masses of various crystal shapes are associated with discharges at different voltages.

Renewed investigations have shown that during the electrochemical activation of the cell, an intermetallic phase of composition Ni_5Cd_{21} is formed on the negative electrode in the presence of reducible nickel oxide (27).

This alloy phase is electrochemically active, but leads to a discharge voltage level which is about 120mV lower than that for pure cadmium.

VARTA has eliminated the appearance of this second step. By special manufacturing procedures it has succeeded in removing the step and its inherent disadvantageous effects.

Cells which, after prolonged trickle charge, develop a second step and, therefore, exhibit reduced capacity can be reconditioned relatively easily. This is achieved by a few normal cycles at the nominal currents, in the course of which the step becomes narrower and eventually disappears. It will, of course, build up again in the event of further trickle charging.

The gradual decrease in the width of the voltage plateau occurring during trickle charge can be reversed. Cells that have been stored for a long time or which have been on trickle charge can undergo a reconditioning charge. This consists charging the cells at the rated current for double the normal time, as a result of which the active masses are completely restored and the cells once more exhibit their original discharge characteristics.

5.6.2 Self-discharge of Sealed Batteries

Alkaline batteries, with nickel hydroxide positive and cadmium negative electrodes, are subject to a systematic self-discharge during open circuit storage. The effect is a gradual decrease in the terminal voltage (Fig. 5/1), and after a time the extractable capacity is significantly lower than that of a freshly charged battery.

Whereas with open cells, the self-discharge is primarily caused by a spontaneous decomposition of the higher valence nickel oxide at the positive electrode, with sealed cells other phenomena play a part because of structural and other factors inherent in the system. Thus the self-discharge observed in sealed cells is caused by a combination of three effects:

1. The decomposition of charged nickel hydroxide by separation of oxygen at the positive electrode, followed by an equivalent reduction at the negatively charged electrode.
2. The building up of an internal self-discharge current by vagrant ions of a redox system ("shuttle").
3. The effect known as "soft short-circuit", caused by penetration of the separator by very small washed out particles of the active mass, or the growth of crystal bridges.

It is quite clear that self-discharge results mainly from a spontaneous decomposition of the higher valence nickel oxide in the positive electrode. After full charge, both electrodes are fully activated. The pressure built up in the free space by the evolution of oxygen at the end of the charge and during overcharge falls exponentially to very low levels, due to the continued chemical process of gas consumption at the negative electrode. With this the conditions of a decomposition of higher valence nickel oxide (pressure-and temperature-dependent) are set. The simplified equations below describe the process:

$$6\,NiOOH + 2e^- \rightarrow 2\,Ni_3O_4 + 2\,H_2O + 2\,OH^- \qquad [5/14]$$

$$2\,OH^- \rightarrow H_2O + \tfrac{1}{2}\,O_2 + 2e^- \qquad [5/15]$$

$$\overline{6\,NiOOH \rightarrow 2\,Ni_3O_4 + 3\,H_2O + \tfrac{1}{2}\,O_2 \qquad [5/16]}$$
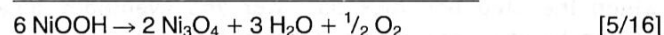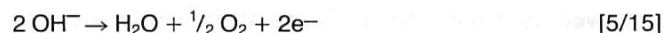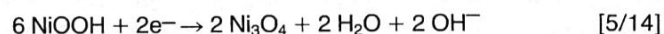
The decomposition is accompanied by evolution of oxygen while leading to thermodynamically stable nickel oxides. It decays exponentially and comes to an end after reaching the condition of stable nickel oxide (approximately 50% residual capacity).

The rate of self-discharge is primarily determined by the geometric proportions of the cell (electrode surface area, electrode separation, electrode activity).

The oxygen given off at the positive electrode reaches the negative, not only via the free space, but also in a dissolved form diffuses through the electrolyte and then brings about the corresponding reduction of an equivalent amount of (charged) cadmium.

Considerable differences in the self-discharge rates exist between sealed mass plate and sintered cells. On thermodynamic grounds, heavy duty cells are more susceptible to self-discharge. Achieving low cell polarization on discharge (e.g. through large internal electrode area) favours the self-discharge rate of the cell in a similar way as the optimum structural parameters (electrode separation, separator permeability, etc.) favour the oxygen reduction.

Besides the part of the self-discharge characteristic brought about by thermodynamic instability, there are also "chemical short circuits". They are an inherent part of a redox system and are accompanied by parasitic side reactions. The best example known, particularly in sealed sintered cells, is the nitrite-ammonia mechanism ("nitrate shuttle", 28). It is apparent when the electrodes contain nitrate as a legacy of the production process. After preliminary reduction of the nitrate ions at the negative electrode [5/17], ammonia is oxidized to nitrite at the positive electrode [5/18], and this is again reduced to ammonia at the negative electrode [5/19]:

$$NO_3^- + 6\,H_2O + 8\,e^- \rightarrow NH_3 + 9\,OH^- \qquad [5/17]$$

$$NH_3 + \tfrac{3}{2}\,O_2 + OH^- \rightarrow NO_2^- + 2\,H_2O \qquad [5/18]$$

$$NO_2^- + 5\,H_2O + 6\,e^- \rightarrow NH_3 + 7\,OH^- \qquad [5/19]$$
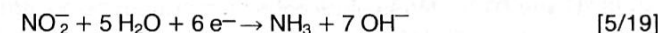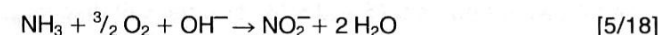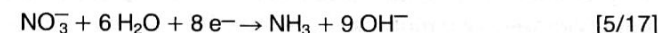
This chemical cycle is maintained until the potential of one of the electrodes is no longer sufficient for the reduction of nitrate and the oxidation of ammonia respectively.

The "soft short-circuit" is characterized by a more or less high contact resistance between electrodes of opposite polarity through direct or indirect connection. This is caused by separated or coagulated particles of the active mass penetrating the separator, and the building up of crystal bridges during a larger number of charge/discharge cycles.

High temperatures not only increase the decomposition rate of highly oxidized nickel hydroxides but also the diffusion rate of the ions taking part in the self-discharge.

On the other hand, at low temperatures the higher valence nickel oxides which determine the capacity are stabilized and diffusion of the vagrant ions is inhibited. Hence, the self-discharge rate falls quickly with decreasing temperature. At —20 °C for example only very low self-discharge rates occur, after the initial fall in capacity over a period of about 6 to 9 months. The rate for mass plate cells is approximately 0.03% to 0.04%, for sealed sintered cells approximately 0.85% per month (Fig. 5/74).
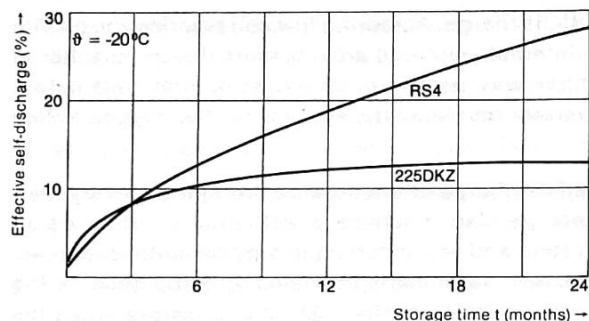
Fig. 5/74:
Effective self-discharge as a function of storage time for DKZ cells (225 DKZ) and RS (RSH) at a storage temperature of —20 °C

The self-discharge increases rapidly at high temperature. As a rule, it can be said that the self-discharge after four weeks storage at + 25 °C is the same as for one week at + 45 °C. At extremely high temperatures, the otherwise very stable mass plate button cells are completely self-discharged within approximately two months.

The following figures 5/75 and 5/76 show the self-discharge characteristics of sealed mass plate and sintered cells at ambient temperatures between —20 °C and 60 °C. Mass plate cells on thermodynamic grounds exhibit markedly better behaviour in this respect.
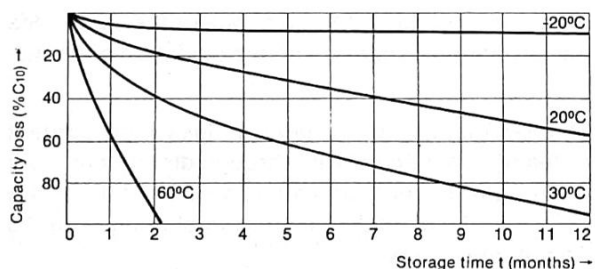
Fig. 5/75:
Capacity loss as % of nominal capacity (C) as a function of storage time for mass plate cells at different storage temperatures
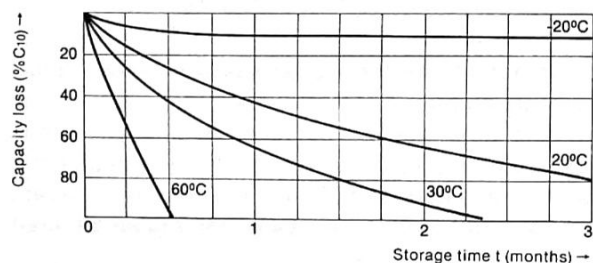
Fig. 5/76:
Capacity loss as % of nominal capacity (C) as a function of storage time for sintered electrode cells at different storage temperatures

5.6.3 Service Life of Sealed Cells

5.6.3.1 Definitions

The long service life of sealed nickel cadmium batteries is one of their most valuable properties. These cells can be stored for prolonged periods without serious permanent loss of capacity. Only a few cycles of reconditioning charge are necessary to restore the cells to full rated capacity after long term storage. The total service life of a sealed cell depends not so much on its age but on the conditions during its use.

Depending on the type of use, the service life is defined as:

1. For continuous charge/discharge service, the number of cycles achieved to a minimum capacity limit, or
2. For trickle charge the operational time to a specified capacity end point.

A cycle is defined here as a complete full cycle. It, therefore, consists of a charge at the current specified for the type of cells concerned, including the recommended charge factor, followed by discharge at the nominal current down to the specified final voltage.

In practice, complete cycles of this kind seldom happen. It is more usual to shallow cycle cells. The I.E.C. standard specified for button cells is given in IEC 509 (1976) (29), and for sealed cylindrical cells in IEC 285-1 (1969) (30). These standards state a 62.5% depth of discharge (related to the nominal capacity) and a charging factor of 1.4. Charge and discharge currents are 1.25 times the nominal current. To meet these specifications, the cells must complete 392 of these cycles, for which the failure criterion is capacity falling below 60% of the rated capacity.

VARTA's sealed batteries are subjected to continual quality control. This ensures that the useful life of VARTA cells meets all the appropriate specifications. A VARTA factory standard for sintered cells specifies a minimum service life of 784 cycles. The number actually reached is significantly higher (section 5.6.3.3) (IEC requires 392 cycles).

5.6.3.2 Factors That Control Service Life
1. Causes of "natural" cell failure.
During the course of their lives, sealed cells undergo changes which reduce their performance. These changes can lead to sudden and total failure, resulting in short circuit or the useful capacity falls below a pre-determined level.

The most important causes of failure are:

— ageing
— short circuit, a soft short circuit because of separator penetration
— formation of carbonate

1.1 The ageing effect is attributed to recrystallization processes, which occur primarily at the negative electrode. Because of gradual agglomeration of crystallites, there is a coarsening of the crystal size during the life of the cell. This progressively increases the "latent" capacity of the negative electrode, meanwhile the charged cadmium in the negative electrode becomes no longer dischargeable. This results in a shift of the cell balance, the useful capacity falls persistently and the ability to perform as a sealed cell is at some point lost. Ageing symptoms are particularly accelerated by permanent operation under high temperatures.

1.2 Short circuit is one of the least welcome causes of failure of sealed cells, and is often caused by penetration of the separator. The cadmium hydroxide in the negative electrode becomes noticeably dissolved in the electrolyte. During the charging process, it is reformed on the negative electrode cathodically, in a bulky and spongy form. High temperatures help these solution and deposition processes. Because the positive electrode also contains cadmium hydroxide (antipolar mass), dissolved cadmium is transported by potential and concentration gradients to the negative electrode, particularly during periods of prolonged overcharge. Particularly good conditions for cadmium deposition are brought about, this time at the positive electrode, by deep discharge (polarity reversal). Cadmium deposition occurs at the positive electrode when a cell is subjected to deep discharge and reverse polarity.

The separator mesh, in close proximity to the active mass, contains cadmium precipitates in spongy or dendritic form so that it becomes increasingly metallized and eventually short circuiting bridges build across the gaps.

Similar conditions are also caused by leaching of the active mass from the electrodes.

1.3 Formation of carbonate after oxidation of graphite or separator only occurs in mass plate cells. During the course of cyclic operation, the oxygen evolved at the positive electrode during charge oxidizes the graphite added to the active mass as a conductor [5/20]. The carbon dioxide so formed reacts with the electrolyte [5/21], also a certain amount of it forms basic carbonate in the active mass. Hence, there forms at the negative electrode for example:

$$x \, CdCO_3, Cd(OH)_2$$
$$(x = 4 \text{ or } 5 \text{ or } 10).$$

$$C + 4\,OH^- \rightarrow CO_2 + 2\,H_2O + 4\,e^- \qquad [5/20]$$

$$CO_2 + 2\,KOH \rightarrow K_2CO_3 + H_2O \qquad [5/21]$$
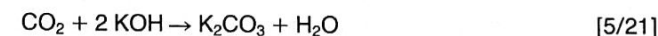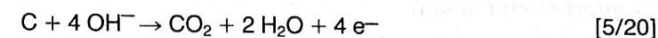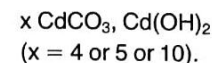
With progressive carbonate formation in the electrolyte and in the active mass inactivation sets in so that the cell capacity is irreversibly affected:

— the internal resistance rises,
— active centres within the electrodes are blocked off by the hydroxicarbonate: passivation of the negative electrode,
— the water and electrolyte content of the cell changes,
— cell balance is upset (decomposition of the negative charge reserve).

The carbonate formation effect is greatly accelerated at high temperatures (Fig. 5/77).

The carbonate effect is less marked with sealed sintered cells. In these, it is caused by oxidation of organic components (separator and expander material).

Fig. 5/77:
Potassium carbonate formation in the electrolyte in relation to number of cycles during cyclic operation of DK series cells (250 DK) and RS types (RSH 4) at different temperatures
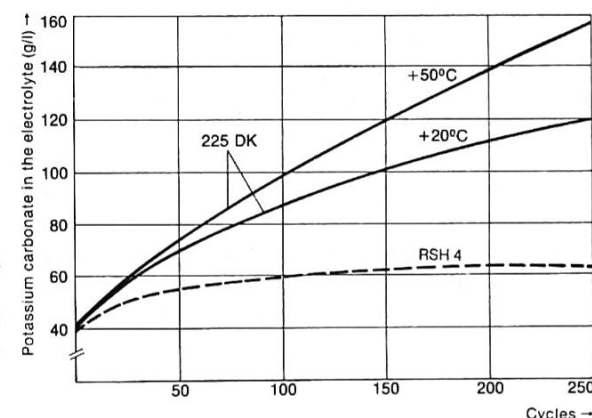
2. Operating conditions that control useful life
The service life of sealed cells actually obtained depends essentially on the operating conditions. The most relevant factors are:

— depth of discharge,
— operating temperature,
— type of charge and charging factor,
— rate of discharge.

2.1 The depth of discharge is the most important factor which determines the life of batteries during cycled operation. Whereas for example, type RS cylindrical sintered cells when discharged by 100% of their nominal capacity, have a useful life of more than 500 cycles.If the depth of discharge is limited to 60%, this increases the number of cycles by more than a factor of two. For discharge depths of less than 30%, the useful number of cycles increases to some ten thousand.

2.2 Effect of temperature on useful life
The longest useful life and the most satisfactory behaviour is achieved by cells which are operated in a normal ambient temperature of about 20 °C. An increase in the operating temperature sharply reduces the working life.

Most general purpose sealed batteries are fitted with polyamide separators. The durability of these is a function of time and temperature. During storage, and particularly during service for long periods at high ambient temperatures, there will be accelerated oxidation and hydrolysis of the separator material. As a result of this, the failure rate rises rapidly and exponentially. At 40 °C, the useful life reduced by more than half.
The choice of the permitted temperature limit is somewhat arbitrary. Cell failure does not immediately occur if the temperature limit is exceeded but the chance of its happening is increased and is dependent on temperature and overcharge conditions.

2.3 Effect of charging on useful life
The increased charging rate does not decrease the useful life. On the contrary, higher charging rates appear to be beneficial to the useful life provided that the charge factors and cut off voltage criteria are followed. On the other hand, constant overcharging does have a detrimental effect on the life of cells. If the periods of overcharge last longer or are repeated more often, then the rate of failure of separators increase, due to the evolution of aggressive nascent oxygen, which also attacks the graphite conductive material. Important consequences of the oxidation processes include:
— increase in nitrate content within the cells, leading to increased self discharge,
— increase in carbonate and hence deactivation,
— loss of negative charge reserve and, therefore, loss of sealed cell performance,
— mechanical breakdown of the separator leading to short circuits.

2.4 The rate of the discharge current has only a minor effect on life of sealed cells provided that the recommended working conditions are followed and the sequence of cycling is not too fast (overheating problems).

3. Mishandling and its effect on the useful life
The effect of regular mishandling and abuse has been discussed in section 5.2.4 (Table 5/1). It is mainly caused by uncontrolled charge and discharge

current, which leads to eventual short circuit, pressure increase, loss of balance, and cell venting.

Failure, caused by mechanical abuse, is fairly common. Excessive mechanical demands (impact, vibration) can break the current collectors. In this way, either the internal contacts between electrode current collectors and cell case can be broken or the external connecting leads (e.g. in the battery) become detached. Special cells designed to withstand severe mechanical environments are subjected to their own series of tests (see Chapters 6 and 9).

Common causes of failure are due to poor soldering or welding techniques. When flow soldering the probability for short circuits is increased. Connections should not be soldered in the vicinity of the sealing, since, due to inadmissibly high temperature generated, irreversibly damaging the plastic components will occur. Cells that have their seals damaged lose their sealed construction and dry out.

There is sometimes during service and during storage a growth of white crystals near the seals. This is caused by minute traces of electrolyte which have managed to creep through micro-capillary passages at the seal and which lead to deposits of potassium carbonate growing by reacting with carbon dioxide in the atmosphere. These white coatings affect neither the useful life nor the electrical performance of the cell, which continues to function as a completely sealed cell.

5.6.3.3 In-Service Capacity of Cycled Sealed Cells
Sealed cells show a continuing decrease in capacity during their time in service. This is caused by the ageing and oxidation processes already described.

For sealed cells which are operating in a purely cyclic service (cycled operation), they can reckon on achieving the approximate number of cycles as shown below:

Table 5/8:
Guide values for the number of cycles to be expected during cycled operation of the various type series

Cells with mass plate electrodes	Series DK	300 - 400
	Series DKZ	400 - 500
Cells with sintered electodes	Series RS and SD	500 -1.000
Monoblock batteries with sintered electrodes	Series 5 M	300 - 400

These guidelines hold good for a normal operating temperature of about 20 °C when the total nominal capacity is inserted at the rated current per cycle. Over the number of cycles stated, a gradual loss of 20%—25% of the nominal capacity should be expected.

However, when shallow cycles (see IEC Standards) are employed, the useful life is extended considerably. Fig. 5/78 gives the capacity characteristics for the operational life of sealed sintered electrode cells based on the IEC Standard (depth of discharge 62.5%; charging factor 1.4). In excess of 2,000 cycles can at times be reached before capacity falls to 60% of nominal, which is the criterion for limit of useful life.
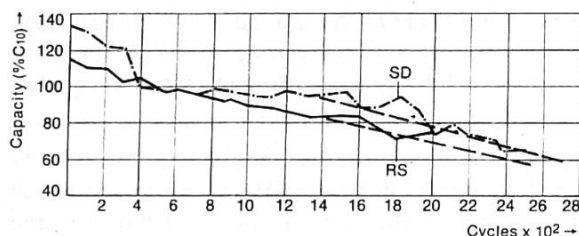
Fig. 5/78:
Main capacity characteristic as % of the nominal capacity related to cycles during cyclic operation to IEC Standard (depth of discharge 62.5%, charging factor 1.4) for RS and SD cells

The figure also shows the effects of various types of cell construction. Thus the considerably greater mechanical stresses applied to coiled electrodes (causing separator penetration) in RS cells have a worsening effect compared with the assembly of interleaved flat electrodes (SD).

Button cells too have a useful life of more than 1000 IEC cycles.

When cells are operating on trickle charge, as rates between 0.01CA and 0.05CA, one can usually reckon on a useful life of about 5 years for a capacity loss of about 30%—40%. Ageing processes play an important part here.

5.6.3.4 Reliability and Failure Rates
The failure frequency under specified operating is commonly used in quantitative statements about the reliability of sealed batteries. The term failure is defined here as the falling below a certain limit (e.g. a stated capacity) of all or the essential functions of a cell, or of intermittent or total internal breakdown such as a short circuit.

Generalized statements cannot be made about the reliability of particular structural elements within the cell because the operation of the system can vary with different conditions of service. Hence the reliability must be based on well defined types of application, and any statements made about it cannot necessarily be transferred from one application to another. Furthermore, for the various arrangements of cells and batteries different parameters apply and these must be considered in reliability reports.

When considering failure rates, it is necessary to distinguish between the following types of service:
1. Cyclic operation
2. Standby power supply

Independent of the type of operation, cells generally have a life of about 5 to 10 years, provided that the recommended operating conditions are followed.

The failure rate is not constant over the whole life of cells, but can be separated into three distinct phases which have the form of the "bath-tub" reliability curve:
— initial period,
— main operating life,
— end of useful life.

The initial period comprises only a small fraction of the total life, and the cell fails almost immediately. The cause is usually that a faulty cell has not been detected upon final check. Some cells, however, have defects which only show up after repeated charge and discharge.

The failure rate stays essentially constant over the useful operating life. For this period, the reliability can be expressed by an exponential function:

$$R(t) = e^{-\lambda t} \hspace{3cm} [5/22]$$

in which R (t) is the reliability, and λ is the failure rate per unit time or per cycle. The duration of the working life depends on the operating conditions concerned, in particular on the ambient temperature and the load.

In the final or end of life period, the majority of cells fail according to a Gaussian distribution function. This period has approximately the same duration as the main operating life.

1. Reliability under cyclic operation
Vast experience in the performance of sealed sintered plate cells has now accumulated. The results presented in the table below refer to cycled operation conforming to IEC Standard 285-1 (current 1.25 x 0.1C; ϑ = 25 °C; depth of discharge 62.5%; charging factor 1.4).

The average useful life under these conditions is about 1500 cycles. The overall capacity throughput to failure for a sealed sintered cell amounts to 950 to 1000 x C.

Table 5/9:
Guide values for the reliability for sealed sintered cells on cyclic service to IEC Standard 285-1

Period	Life	Failure rate (Failure/cycles)	Total failures
Initial	Approx. 30 cycles	5×10^{-5} to 10^{-4}	Approx. 0.2%
Main	Approx. 1000 cycles	Approx. 10^{-4}	Approx. 10%
End of Life	At least 1000 cycles	Approx. 10^{-3}	Approx. 100%

2. Reliability under standby operation

The results shown in Table 5/10 refer to a standby power supply. The average working life for the stated conditions is about 150,000 hours, during which time the capacity achieved equates to approximately 3000 x C.

Table 5/10:
Guide values for the reliability of sealed sintered cells on trickle charge at $0.2C_5A$ at 25 °C

Period	Life	Failure rate (failures/h)	Total failures
Initial	Approx. 3 months	Approx. 5×10^{-7}	Approx. 0.1%
Main	Approx. 100,000 h	Approx. 5×10^{-7} to 10^{-8}	Approx. 5% to 0.1%
End	Approx. 100,000 h	Approx. 10^{-5}	Approx. 100%

5.7 Development Trends

Due to their excellent properties, sealed nickel cadmium batteries are employed in all fields of electrotechnology. The progressive development in research and in manufacturing has, in recent years, brought about a great number of new applications, thus for example, their use in space travel likewise, in the leisure industry. In consequence, the "classic" sealed battery has sometimes not been equal to the demands and has been adapted to specific applications as they have occured. This brought in a number of different types having new limits of operating conditions widened from those of the established types as became necessary. Disregarding those properties which have been improved so that they can meet almost all reasonable demands, there are still several factors which limit these applications.

The most important of these are directly dependent on the temperature and pressure conditions within the sealed battery. Capacity and size and hence the heat radiating surface must be interrelated in definite proportions in order to prevent overheating during charge. Therefore, there is a present day limit to a capacity of 15Ah to which sealed cells can be charged without special systems.

The cells internal pressure is another point to be watched. Normally, the working pressure is quite small. However, with cells having large surface area, the battery case can be distorted.

Further restrictions are necessary when banks of cells are used. The interconnection of cells to form batteries requires as small as possible spread in the capacity of the individual cells. Cells with low capacities would not only limit the discharge of the battery, but in extreme cases, they would become reverse polarized, fail, and thus bring about the total failure of the whole battery. This danger exists particularly in the latter part of the useful life, the period known as the "run-down" (section 5.6.3.4).

In spite of all the developments and advances made in rechargeable battery systems, sealed nickel cadmium cells will maintain their place in the battery market and, in the future, even extend it. In addition to the efforts made by manufacturers to improve reliability to bring better quality products on to the market at economical prices, certain trends stand out, to which future developments will be related:
— Raising the storable energy relative to cell volume and weight by the development of smaller more compact cell units with optimum geometry and with the lowest possible internal resistance.
— Increased flexibility to satisfy special applications, at high temperatures, low current loads, minimal self discharge, and very efficient sealing.
— There is a special interest in the development of a maintenance free sealed unit of high capacity up to 100Ah.
— The trend towards minimum size is equally important, particularly cells for use on printed circuits, in electronic apparatus and medical aids.

6.1 General Physical Properties

In common with all electrical components, sealed nickel cadmium cells possess important physical properties in addition to their electrical characteristics.

Concerning measurements and weights, there are IEC Standards and manufacturers' specifications which apply to all sealed nickel cadmium batteries. The data relevant to each cell type is available in separate leaflets. The following special features of sealed nickel cadmium batteries should be remembered:

1. Breathing tolerances: There is a change in size during charge and discharge, particularly in the length of button cell batteries; with rectangular cells, the broad sides tend to bulge. This should be taken into account during battery designs and installation (section 5.2ff).

2. In spite of the sealing, there are preferred operating positions for certain types, for example, cells with safety valves should be installed as far as possible upright.

3. Certain precautions should be observed when sealed nickel cadmium cells are stored. As far as possible, only dry and frost-free rooms should be used for their storage. Care should be taken to prevent metal objects from falling on the cells.

4. Because sealed nickel cadmium batteries contain materials which, if improperly handled, i.e. mechanical destruction of the cells, will escape and which can cause health hazards, unusable cells should not simply be thrown away as domestic refuse or incinerated, but should be disposed of safely or returned to the trade as scrap metal.

5. Sealed nickel cadmium batteries should not be subjected to any mechanical distortion. There is a danger of short circuit, with the possibility of heating, which can lead to an outbreak of fire.

6. Regulations which lay down rules for batteries and battery installations (e.g. VDE 0510) are to be considered mandatory for every application of sealed nickel cadmium batteries. In addition, further regulations apply to apparatus in which sealed nickel cadmium batteries are used. Because many of the properties of nickel cadmium batteries — mechanical as well as electrical — can vary quite widely during normal temperature changes, climatic conditions, or because of other factors, this topic is covered in detail in section 6.2 below.

6.2 Environmental Factors

6.2.1 Normal and Abnormal Use

It is possible to specify aspects of a structural component which is obviously necessary for its "normal function"; on the other hand, "abnormal" can be considered as referring to certain limiting values that may be approached or exceeded. Hence for every battery application, it is necessary to define the limits of normal use, or what can be achieved in practice, and the battery manufacturer states the permissible operating conditions. In each case, there must be compatibility between the requirements and the component. To this end, certain methods can be used to simulate the environment, and these can be laid down as a series of standard tests.

6.2.2 Specifications and Standards

Table 6/1 lists a series of standards for the testing of components and apparatus based on environmental requirements. Although this table does not include all the known standards, it does embrace more than 90% of all battery applications.

We can generally differentiate between two large groups of requirements: mechanical and climatic, in which the latter shall include the effects of high altitude as far as total vacuum conditions in extra-terrestial space.

In the standard tests, some unification has been achieved so that the normally occurring environmental effects are dealt with separately. Thus the mechanical stresses have been classified as vibration, impact (shock), and constant (linear) acceleration, even though the most complex overlapping can occur during transport and operation of batteries on the earth's surface and in the airspace.

For the climatic tests, there are occasions when two of the above factors have to be joined to form a third, because otherwise the true objective cannot be attained; such examples occur during tests to simulate the thermal and vacuum conditions under which space travel apparatus has to operate, or temperature — humidity — altitude tests on military and air transport equipment.

6.2.3 Measures to Meet Environmental Requirements

As a general rule, structural components would be much too expensive if they were designed to meet all possible environmental requirements simultaneously.

Therefore, the designer limits the problem by meeting the normal requirements and leaves it to the user to moderate or to neutralize the effects of the environment on the components through the use of special protective measures. If this procedure does not satisfy the needs of the user, as, for example, with space travel or military purposes, then special developments

Table 6/1:
Environmental requirements and the relevant tests and standards

Type		MIL Standard No. Method		DIN Standard No. Sheet		IEC
Mechanical Environmental Requirements	Linear acceleration	810 C	513.2.	40046	21	68
	Vibration	810 C	514.2.	40046	8	68
	Mechanical impact	810 C	516.2.	40046	7	68
	Acoustic level	810 C	515.2.			
	Gunfire vibration in aircraft	810 C	519.2.			
Climatic Environmental Requirements	Low pressure	810 C	500.1.			
	High temperature	810 C	501.1.			
	Low temperature	810 C	502.1.			
	Temperature shock	810 C	503.1.			
	Temperature altitude	810 C	504.1.			
	Solar radiation	810 C	505.1.	53386 53387 53389		
	Rainfall	810 C	506.1.	40053 53386 53387		
	Humidity	810 C	507.1.			
	Fungal growth	810 C	508.1.			
	Salt spray	810 C	509.1.	40046 50021	11	
	Dust (fine sand)	810 C	510.1.			
	Explosive atmosphere	810 C	511.1.			
	Immersion	810 C	512.1.			
	Space simulation	810 C	517.1.			
	Temperature-humidity-altitude	810 C	518.1.			
	Industrial atmosphere			50018		50

and designs have to be achieved by the battery manufacturer. These will naturally raise the price of the batteries considerably, even when no change in the electrical characteristics is needed.

6.2.4 Mechanical Environmental Factors

6.2.4.1 Effects on Sealed Batteries
The essential constructional details of all sealed nickel cadmium cells in all the various series are described in section 7.1.

When sealed batteries are subject to vibration, the electrodes can vibrate against each other, and against the case. The electrodes can, therefore, hammer against the adjacent separators and partitions, and stress the connectors. Damage to the electrodes (abrasion), to the separator (perforation), the current collectors (cracks through bending and torsion), to the welded joints (breaking off, tearing of the solder tags) or the terminal connectors and their insulators, and the sealing can be the result. If the batteries are being discharged when the vibration occurs, then under some circumstances there can be internal resistance fluctuations which in turn cause a superimposed "noise voltage" on the output.

Various kinds of impact give rise to similar effects, depending on the type of cell construction; short and sharp blows are less damaging than blows of longer duration with less acceleration. Constant acceleration is, as a rule, not so damaging as the rapid changes in acceleration caused by vibration, provided that there is no actual ejection of the electrolyte from the separator; this would have the effect of temporarily raising the internal resistance of the cell and hence would deteriorate its electrical performance.

6.2.4.2 Mechanical Stresses
Mechanical stresses generated during motion occur during a wide range of applications in the fields of land, sea, and air transport including rocket propulsion. Batteries can either be components in the vehicles themselves, or they can be used in the apparatus carried. Important shocks can also arise when the apparatus have been handled roughly or have been dropped.

Linear acceleration occurs when the vehicle gains velocity or is braked, or follows a curved path. Such acceleration can have detrimental effects on the batteries. Table 6/2 gives the range of the accelerations involved.

The values given above can be withstood by batteries during tests; apart from the figure for free fall, all the other values are about 50% greater than the accelerations met during service.

It should be noted that in the case of rockets, besides the accelerations along the trajectory, there can be centrifugal acceleration because of spin; any such acceleration can be calculated by use of the standard equations of motion.

Occurrence	Acceleration up to
Free fall	$1\,g \approx 10\ m/s^2$
Helicopters	10.5 g
Aircraft	13.5 g
Manned rockets	13.5 g to 27 g
Ground launched unmanned rockets	9 g to 45 g

Table 6/2:
Linear acceleration. Maximum value of acceleration for various types apparatus (based on MIL-STD 810 C)

Vibrations usually originate from the general propulsion of the vehicle; they can however, in exceptional cases, result from other causes (e.g. gunfire vibration on board military aircraft). The effect of these vibrations on the batteries which are part of the equipment can be mitigated by the use of vibration-proof mountings; nevertheless, this will not normally be necessary because of the extremely high resistance of cells to such vibrations.

Sinusoidal and non-recurrent vibrations are the most important types involved here. The motion of the object under *sinusoidal vibration* is given by the equation

$$A\,(t) = A_0 \cdot \sin \omega\, t \qquad [6/1]$$

in which A_0 is the maximum displacement in one direction, or amplitude of the vibration, $2\,A_0$ is the peak-to-peak value (DA), and $f = \omega/2\pi$ is the frequency. From the velocity

$$\frac{dA(t)}{dt} = \omega \cdot A_0 \cdot \cos \omega\, t \qquad [6/2]$$

the acceleration is obtained, thus

$$\frac{d^2A(t)}{dt^2} = -\,\omega^2 A_0 \cdot \sin \omega\, t \qquad [6/3]$$

The maximum value of the acceleration occurs when
$$\sin \omega\, t = 1 \qquad [6/4]$$

i.e. $b_{max} = -\,4\pi^2\, f^2 \cdot A_0$ $\qquad [6/5]$

For example, if an acceleration of b = 1 g is to be applied to an object with a frequency of 5 Hz, then its motion must have a peak-to-peak amplitude of 2 cm, thus:

$$\tfrac{1}{2}\, DA = A_0 = \frac{10}{4\,\pi^2 \cdot 25}\, m = 1\ cm \qquad [6/6]$$

The strength of the unit under test with *sinusoidal vibration* is usually measured by starting at about 5Hz, increasing the frequency to a maximum of 2000Hz, and decreasing again. The connection between acceleration and frequency is described in section 6.2.4.3.

Under *complex vibrations* the object follows a stochastic motion, as when a noise consisting of several different frequencies occurs. Here the individual frequencies do not occur one after another but all at once. Their spectrum may range from 20Hz to 2000 Hz, over which range each component frequency has its own amplitude and the whole series forms a spectrum, which can be shown pictorially in the form of an envelope enclosing all the peak values, and based on values of g^2 per Hz. Further details can be found in section 6.2.4.3. A vibration test consists of coupling a vibration generator to the test specimen for a specified period.

Some vibrations, not generally important, but which should be considered for the sake of thoroughness, include "acoustic noise" and "aircraft gunfire vibrations". Neither type is of great significance for sealed nickel cadmium cells. They are not "acoustically sensitive" components because they have too small a ratio of surface area to mass and too high internal damping, so that they are not sensitive to acoustic impulses; besides this they can always be mounted in aircraft in such a way that gunfire vibrations are of less importance than other types.

Mechanical impact or *shocks* can arise from a great number of different causes and can affect the interior of the battery, its case, internal mountings, and connections to the terminals, its clamps in the battery carrier, and the mounting brackets of carriers themselves. The impulses can occur during transport, because of acceleration and deceleration, through handling during service, when rocket stages are separated, during rail transport, as a result of parachuting of supplies from aircraft, or in lift-off experiments. Corresponding to these there are many different types of simulation tests, of which the most important are the half-sine shock pulse, the sawtooth acceleration pulse, and the synthetic pulse. Of these various methods, the half-sine shock pulse is described in more detail in section 6.2.4.3.

6.2.4.3 Test Methods
Linear acceleration is simulated mainly by mounting the test object on the beam of a centrifuge, and in such a way that the desired acceleration is applied via the approximate centre of gravity. The objects are tested with the acceleration acting in turn along the directions of the arrowheads in Fig. 6/1, which designate the various axial directions.

Fig. 6/1:
Definition of axial directions used in mechanical tests
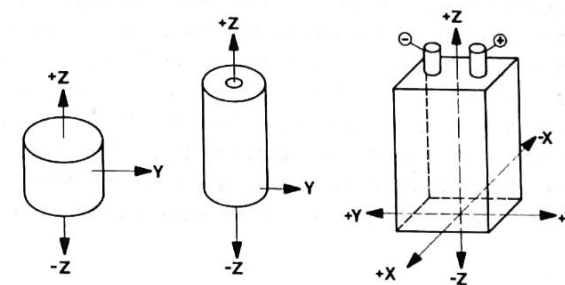
The centrifuge is accelerated from rest until the required acceleration is reached, run for the prescribed time, and then switched off. During the period of constant angular velocity the cells under test are checked for fault-free electrical performance (open-circuit and on-load voltages). Examples of the accelerations used are given in Table 6/2.

Sinusoidal and *complex or random vibrations* are simulated on a vibration machine or table. Electrodynamic methods are mostly used. Fig. 6/2 shows a group of four rectangular nickel cadmium batteries on such a vibrating table, undergoing vibration tests in the X axis direction. Because vibrations are always acting in both positive and negative axial directions, with cylindrical cells two, and with rectangular cells three, sets of consecutive measurements must be made for each rate of acceleration.
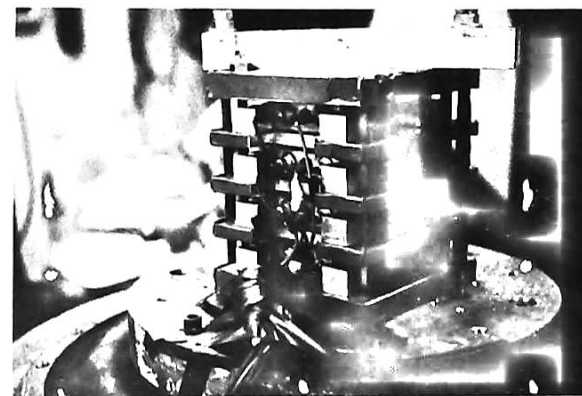
Fig. 6/2:
Four rectangular nickel cadmium cells type SD 15 K in an acceleration test jig on a vibrating table (testing along the X axis)

For sinusoidal excitation, there is a choice between the two possibilities shown in Fig. 6/3 and 6/4. These methods show clearly the relationship between displacement and acceleration derived in section 6.2.4.2. At low fre-

quencies, the displacements obtained would be too big for satisfactory verification of the accelerations to be reached at higher frequencies. The acceleration is taken at constant peak-to-peak amplitude through the whole frequency range until the desired loading (measured in g) is reached and this acceleration is then held constant for further increases in frequency by reducing the peak-to-peak amplitude. This procedure is based on the fact that at low frequencies the cell reinforcing components would not sustain the very high displacements theoretically needed for the amount of acceleration concerned. It is common practice to start the test from a certain frequency in the spectrum as shown by the broken line in Fig. 6/4; this is permissible when it is known that no powerful forces arise at higher frequencies.
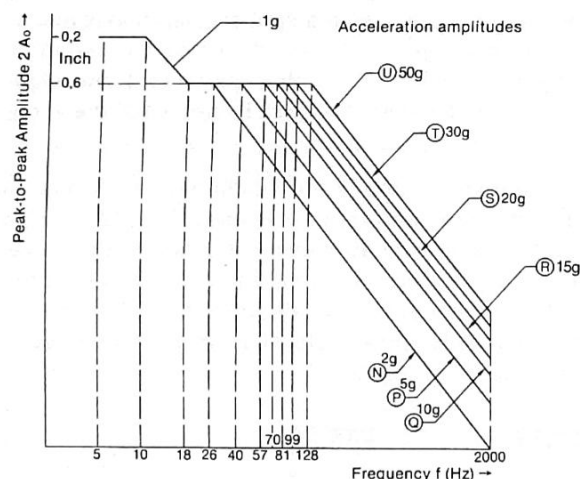
Fig. 6/3:
Vibration envelopes for sinusoidal tests plotted as peak-to-peak amplitude versus frequency, based on MIL-STD 810 C, Method 514.2 for ground launched rockets (equipment category e)
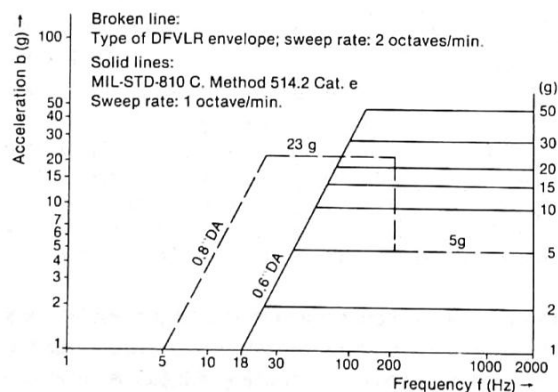
Fig. 6/4:
Vibration envelope of acceleration versus frequency as used in space technology. Broken line gives test results for DFVLR at Köln-Porz for communication satellite system

The letters given in Figs. 6/3 and 6/4 correspond to those in Table 6/3, which represent examples of average motion to which these test accelerations refer.

Table 6/3:
Sinusoidal vibration. Maximum acceleration amplitudes, test durations, and sweep frequencies for apparatus in various types of rocket (based on MIL-STD 810 C and NASA Specifications)

Vehicle Type: Rockets	Type of Mounting*	Vibration Envelopes In Fig. 6/4	Duration of test — min. per axis	Sweep Rate 5-2000-5 Hz minutes
All stages with any thrust except booster stage (after MIL)	a	P or Q	30	20
	b	P, U	30	20
	c	N	30	20
Booster stage with thrust (after MIL) up to 250 000 lbs	a	Q or R	30	20
	b	Q or R	30	20
	c	N	30	20
250 000 to 500 000 lbs	a	R or S	30	20
	b	R or S	30	20
		N	30	20
Above 500 000 lbs	a	T or U	30	20
	b	T or U	30	20
	c	N	30	20
Pay load stage (NASA)	—	broken line	10	9

*Type of mounting: a = without vibration isolators, b = with vibration isolators, to determine resonance, c = with mounting, but test without vibration isolators.

For *complex vibrations*, the log-log diagram shown in Fig. 6/5 gives the power spectral density plotted against frequency. For every frequency, there is a power value W in g^2 per Hz. The effective acceleration b_{eff} is found from the envelope representing the acceleration, using the formula

$$b_{eff} = \sqrt{\int_{f_1}^{f_2} W(f)\, df} \qquad\qquad [6/7]$$

in which W (f) is the power spectral density for the frequency concerned in g^2 per Hz. The pairs of letters shown in Fig. 6/5 correspond to those given in Table 6/4, which gives examples of acceleration tests for different types of rocket.
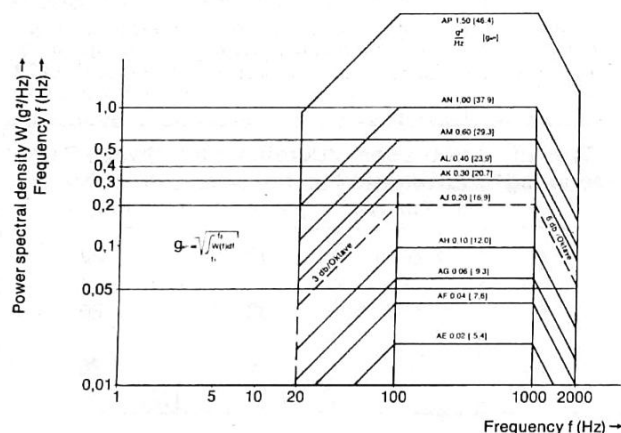
Fig. 6/5:
Noise vibration diagram showing power spectral density W plotted against frequency f, based on MIL-STD 810 C, Method 514.2 for ground launched rockets (èquipment category e). The broken line envelope refers to a test on the DFVLR at Köln-Porz for communication satellite systems

Shock or impact stresses are simulated with a shock tester, in which the object under test is fastened to a carrier and falls on a test bed or plate, or a hammer blow is delivered against the object which is mounted on a sliding table.

The shock (retardation/acceleration) is mostly transmitted via a rubber base-plate; with vertical shock tests a sand-bed is sometimes used. Only sinusoidal excitation will be described here; Section 6.2.4.4 gives results of tests on sealed nickel cadmium batteries. Fig. 6/6 shows the general profile of the half sine shock pulse defined in MIL-STD 810 C. Table 6/5 gives the values of peak amplitude A and the specified duration D for different types of apparatus.
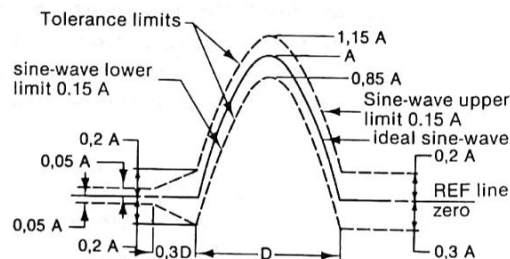
Fig. 6/6:
Half-sine shock pulse (based on MIL-STD 810 C, Method 516.2)

Table 6/4:
Complex vibration. Maximum values for the power spectral density and duration of test for different types of rocket (based on MIL-STD 810 C and NASA specifications)

Vehicle type: Rockets	Type of Mounting*	Envelope Shown in Fig. 6/5	Duration of test — min. per axis
All stages with controlled thrust except booster (after MIL)	a	AE, AF or AG	30
	b	AE, AF or AG	30
	c	EA	30
Booster stage with thrust (MIL) up to 250 000 lbs	a	AH, AJ or AK	30
	b	AH, AJ or AK	30
	c	EA	30
250 000 to 500 000 lbs	a	AK, AL or AM	30
	b	AK, AL or AM	30
	c	EA	30
Above 500 000 lbs	a	AM, AN or AP	30
	b	AM, AN or AP	30
	c	EA	30
Pay load stage (after NASA)	—	broken line	4

*See footnote to Table 6/3

Equipment	Test	Peak Value A (x 10 m/s²)	Duration (ms)
Aircraft Equipment	"Basic Design"	15	11
	"Crash Safety"	30	11
	"High Intensity"	100	6
Ground Equipment	"Basic Design"	30*	11
	"Crash Safety"	60	6
	"High Intensity"	100	6

Table 6/5:
Shock requirements for half-sine shock pulse (Fig. 6/6) peak value A and specified duration D for different equipment and tests (based on MIL-STD 810 C) (3 pulses per axis usual)

* This value can be reduced to 20 for equipment mounted in trucks.
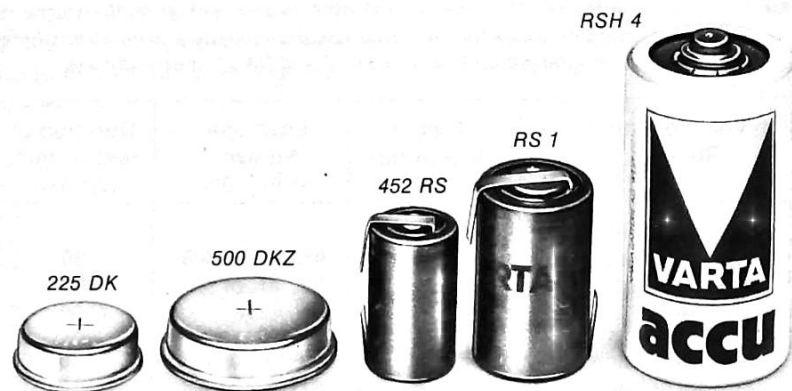
Fig. 6/7:
Rotation symmetrical cells from VARTA's sealed nickel cadmium battery production
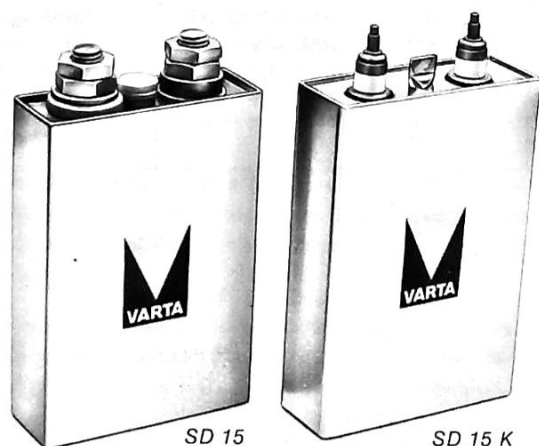
Fig. 6/8:
Rectangular cells from VARTA's sealed nickel cadmium battery production

6.2.4.4 Typical Results From Mechanical Tests on Sealed Nickel Cadmium Batteries

Tables 6/7 to 6/10 give the results for VARTA sealed nickel cadmium batteries tested in accordance with the methods described in sections 6.2.4.2 and 6.2.4.3. The batteries to which these tables refer can be regarded as typical of the VARTA series; Fig. 6/7 and 6/8 show their shapes and Table 6/6 lists some details of important structural factors.

Table 6/6:
Typical cells from VARTA's sealed nickel cadmium battery series, together with data on their design and construction

No.	Series	Type	Capacity Ah	Base Surface (mm $\varnothing$, mm)	Total height (mm)	Case	Sealing	Weight (g)
1	250 DK	Button cells with mass plate electrodes	0.250 $C_{10}A$	25.1	8.8	Nickel-plated steel	Polyamide Gasket	11.8
2	600 DKZ		0.600 $C_{10}A$	34.4	10.0	Nickel-plated steel	Polyamide Gasket	26
3	452 RS	Cylindrical sintered electrode cells	0.450 C_5A	17.2	28.0	Nickel-plated steel	Polyamide Gasket	19
4	RS 1		1 C_5A	23.0	35.7	Nickel-plated steel	Polyamide Gasket	41
5	RSH 4		4 C_5A	33.5	61.0	Nickel-plated steel	Polyamide Gasket	91
6	SD 15	Cylindrical sintered electrode cells	15 C_5A	30x77	126	Nickel-plated steel	Polyamide Gasket for Negative	780
7	SD 15 K		15 C_5A	30x77	130	Stainless Steel	Pillar Metal Ceramic Terminals	660

Type	Acceleration in multiples of g ($g \approx 10$ m/s^2) in the axial direction					
	+x	-x	+y	-y	+z	-z
250 DK	40	40	40	40	40	40
600 DKZ	40	40	40	40	40	40
452 RS	40	40	40	40	-	-
RS 1	40	40	40	40	40	-*
RSH 4	40	40	40	40	40	-
SD 15	40	40	40	40	40	-*
SD 15 K	40	40	40	40	40	-*

Table 6/7:
Typical performance of sealed nickel cadmium batteries made by VARTA under linear acceleration (Duration of test: 2 minutes)

* Mounting shall be such that this acceleration does not occur

Table 6/8:

Typical performance of VARTA sealed nickel cadmium batteries under sinusoidal vibration (limit values for SD 15 and SD 15 K types).
— *based on Fig. 6/4, broken line graph, i.e. 0.8 DA, for increasing frequency from 5Hz until reaching greatest acceleration amplitude, reduced acceleration from 200Hz to 2000Hz. The same sequence while reducing the frequency.*
— *Sweep rate: 2 octaves/minute*
— *Duration of test: at least 9 minutes*

Type	Axis	Acceleration in multiples of g (g $\approx$ 10 m/s^2)	
		Max amplitude to 200 Hz (g)	Reduced amplitude from 200 to 2000 Hz (g)
250 DK	x	-	-
	y	40	15
	z	40	15
600 DKZ	x	-	-
	y	40	15
	z	40	15
452 RS	x	-	-
	y	30	7
	z	40	15
RS 1	x	-	-
	y	30	7
	z	30	7
RS 4	x	-	-
	y	30	7
	z	30	7
SD 15	x	35	10
	y	35	10
	z	35	10
SD 15 K	x	40	15
	y	40	15
	z	40	15

The tests concerned were carried out in the following way:

1. To improve the accuracy of the tests groups of at least four batteries were used, mounted together in a fixture.
2. During the critical stages of the tests, the batteries had electrical loads applied and the cell voltage was measured. In addition, the open circuit voltage was measured before and after the test to, at least, three figure decimal places.

3. Concerning the above, when carrying out the individual tests, the following applies:

For *linear acceleration* tests, which can be carried out at 40 g for all groups, the maximum speed of the centrifuge is reached within 2 minutes, is held constant at 40 g for 2 minutes, and the run down period is also 2 minutes.

Table 6/9:

Typical performance of VARTA sealed nickel cadmium batteries under complex vibrations (limit values for SD 15 and SD 15 K types)
— *based on Fig. 6/5 curve*
— *duration of test at least 4 minutes per axis*

Type	Axis	Highest value of power spectral density (g^2/Hz)	Effective value required (g$_{eff}$)
250 DKZ	x	-	-
	y	0.40	24.0
	z	0.40	24.0
600 DKZ	x	-	-
	y	0.40	24.0
	z	0.40	24.0
452 RS	x	-	-
	y	0.30	20.7
	z	0.40	24.0
RS 1	x	-	-
	y	0.30	20.7
	z	0.30	20.7
RSH 4	x	-	-
	y	0.30	20.7
	z	0.30	20.7
SD 15	x	0.28	-
	y	0.28	20.0
	z	0.28	20.0
SD 15 K	x	0.40	24.0
	y	0.40	24.0
	z	0.40	24.0

The shock test results, obtained with a horizontal plane shock machine (sliding table, against which a hammer blow is struck), are given in Table 6/10.

In *sinusoidal vibration* tests, the relationship between acceleration and frequency can be found by reference to the broken or straight line in Fig. 6/4. The broken line is more severe and can be considered as determining both variables for nickel cadmium batteries, and Table 6/8 is based on the values given by the table.

The results of sinusoidal and complex vibration tests as given in Tables 6/8 and 6/9 show that the work can be organized so that the time between tests is minimized, thus:

— either for each axis the same test (sine or complex) is carried out at the next higher load,
— or while maintaining the same axial direction carrying out the other test,
— or the cell is moved into the next axial position for the same test at the same or increased loading.

Basically, it is desirable to increase the sine and complex vibration levels in line with each other so that limiting loads are approached with the same specimen.

Table 6/10:
Typical performance of VARTA sealed nickel cadmium batteries during shock tests.
— shock pulse as shown in Fig. 6/6
— 3 pulses per axis in both positive and negative axial directions

Type	Axis	"Crash Safety"		"High Intensity"	
		Amplitude (g)	Duration (ms)	Amplitude (g)	Duration (ms)
250 DK 600 DKZ 452 RS RS 1 RSH 4	+y -y +z -z	30	11	100	6
SD 15 SD 15 K	+x -x +y -y +z -z	30	11	100	6

Values given are valid for all axial directions

6.2.4.5 Evaluation of Test Runs and Results Obtained

It is fundamentally true to say that a battery which has to be tested for ability to withstand some mechanical stress:
— must neither have its electrical function disturbed,
— nor in one way or another should have its function or useful life adversely affected.

Whilst its ability to perform under the first condition can be easily tested, meeting the other requirement can as a rule only be tested by a real endurance test rather than a simulated one. The results quoted in section 6.2.4.4 are valid for only a relatively small number of tests under stress conditions. Generally, there are no firm rules on procedures for transferring these tests results across to assessment of long term performance. It is, therefore, left to the user, or the specialist in the application concerned, to decide to what extent the values given in Tables 6/7 and 6/10 satisfy his operational requirements.

6.2.5 Climatic Environmental Factors

6.2.5.1 Effects on Sealed Batteries

At this point, it is pertinent to refer to the constructional features of nickel cadmium batteries which are stated in section 7.1. Additional information can also be found in Table 6/6, which gives particulars about the external parts which are exposed to climatic influences. For details of electrochemical and other technical aspects, reference should be made to the detailed discussion of the effects of extreme climatic temperatures already given in sections 5.4.8, 5.5 and 5.6.

The various ways in which climatic effects can arise have been detailed in Table 6/1. As a start, it can be said that batteries can be exposed without protection to these effects for relatively short durations, but that in many cases, by special precautions, they can be kept ready for service over a long period. Only in a very few cases are special types necessary, namely in respect of hermetic sealing, extremes of temperature, and long storage periods.

Crystal growth can occur in the sealant area as a consequence of *low pressure*, and in some circumstances can lead to the drying out of the cell.

At *high temperatures*, distortion of plastic parts can occur, and they may become discoloured; in addition to the electrochemical processes are accelerated, chemical compounds can decompose (e.g. decomposition of higher nickel oxide), self discharge is faster, and the separator can age and be prematurely destroyed. At *low temperatures*, various kinds of shrinkage can affect the component parts and lead to damage, and loss of elasticity in gas-

kets can result in seal failure, electrochemical processes are retarded, charge and discharge processes are impeded or even prevented, at temperatures below —40 °C ice forms in standard cells from the water in the electrolyte.

Similar phenomena to those already described occur during *temperature shock* and *temperature altitude tests*. *Solar radiation* can cause reversible as well as permanent changes, and set up mechanical stress in the cell through uneven heating which can ultimately lead to failure. Permanent changes include colour fading, ageing, and cracks in plastic components.

Rain and *humidity* can have corrosive effects on the cell case. Hence, suitable precautions should be taken when housing cells to protect them from rainfall and floodwater. The effects of humidity should be reduced to a minimum and, if necessary, measures taken to exclude it.

Fungal growth and *salt spray* must be excluded from unprotected cells due to the danger of an external short circuit. On the other hand, dust is not harmful, provided that it is dry. The presence of *explosive gasses* does not harm sealed nickel cadmium batteries, and the same comment applies to *immersion* in neutral or weakly conductive solutions, as long as they are dried immediately. *Space application* demand long term use, which requires special types of cell, for example, the SD 15 K cells, but for short period use, the other models listed in Table 6/6 will be suitable.

6.2.5.2 Occurrence of Various Climatic Factors

During air transport, low pressure, high and low temperatures can occur, also during storage, particularly when protective packaging has been removed. Temperature shock arises during ejection of apparatus from high altitudes, when the ambient pressure will also change. Solar radiation, rainfall and humidity are general climatic influences which can be expected nearly everywhere, and against which only suitable packaging can be effective. Fungal growth, salt spray and similar factors can likewise be generally combated by packaging. For space applications, the vacuum and solar radiation effects are overriding, together with the cooling effect of space; because there can be no convection in a vacuum, thermal problems have to be solved by heat conduction and radiation. The batteries should be so well hermetically sealed that they do not have the smallest leak (leak rate $< 10^{-10}$ bar $\cdot$ l $\cdot$ s $^{-1}$).

6.2.5.3 Test Methods

Only recommendations for meeting the test requirements will be discussed here; cells under test should be handled in accordance with the various test methods described in MIL-STD-810 C. The figures given will indicate how well the cells under test will withstand the forces applied.

During *temperature tests*, the cells are stored at temperatures down to — 57 °C and are then put into operation at the lowest specified temperature. For *temperature shock* tests, they are held at 71 °C and are then transferred to a chamber at —57 °C, left there until temperature equilibrium has been reached, and then returned to the first chamber, and so on.

With *temperature altitude tests*, the pressure change corresponds to an altitude change from 0 to 30000 m, and the temperature range is from —62 °C to 150 °C and above.

Solar radiation proceeds cyclically and the tests are based on more than 14 hours sunshine per 24 hours; the ambient temperature is maintained at 49 °C for 6 hours. Not included here are fungal growth, salt spray, dust, explosive atmospheres, immersion, and space simulation. In the *humidity test*, the cell is subjected to temperature and humidity changes between 65 °C max at 95 % relative humidity and 23 °C at 50 % relative humidity.

7. Type Range, Assembly and Production of Sealed Nickel Cadmium Batteries

7.1 Type Range and Construction of Sealed Nickel Cadmium Batteries

7.1.1 Explanation of Type Numbers

The original type number system used for the various types of cell has been expanded over the course of time because of the introduction of new types as a result of development and in response to market demands. In addition, because of the widespread familiarity with the type numbers of certain cells, any new system of classification and numbering would have been out of the question.

Each type number must give information on the type of construction, type of electrode, the series and the electrical specification of the cell or battery concerned if the meaning of the combinations of letters and numerals used is to be understood.

The letters used to designate the types of construction have the following significance:
D — Sealed
K — Button Cell
Z — Twin Electrodes
O — Oval Cell
R — Cylindrical Cell (Round Cell)
S — Sintered Electrode Cell
P — Cell with Pressed Negative Electrode
H — Cell for Extremely High Rates of Discharge
X — Cell for Extremely High Discharge and Charge Current
T — Cell for High Temperatures
M — Monoblock Battery

Because button cell (K) and cylindrical cell (R) models are designated by letters, it is superfluous to use another letter for rectangular cells. Likewise, for the type "cylindrical cell with sintered electrodes (RS)" the letter "D" is omitted so as to make the sequence of letters connected with the application (e.g. P, H, X and T) more obvious.

The numerals used in conjunction with the type letters indicate the capacity of the cell, i.e. the amount of stored energy.

Numerals in front of the letters give the capacity in milliampère-hours (mAh), numerals behind give the capacity in ampère-hours (Ah).

When the figure "1" is added to the end of the capacity figure, it indicates a cell which has a different type of contact cap from the basic type, therefore, making it interchangeable with equipment size dry cells. It has the capacity of the basic type.

Example:

Cell 501 RS — Cylindrical cell with sintered electrodes, interchangeable with dry batteries of the same size, capacity 500mAh (basic type 500RS).

Because the nominal voltage of a sealed nickel cadmium cell is 1.2V in all cases, this information is omitted from the cell code.

Table 7/1 is a product chart showing symbol letters designating various combinations of type of structure, electrode type and model.

Table 7/1: *Product Chart*

Model	Electrode Group	Series	Capacity
Button Cells	Mass Electrodes	DK/DKO	10—1000 mAh
		DKZ	160—1000 mAh
Cylindrical Cells	Sintered Electrodes	RS RSH RSX	0.1—7Ah
Rectangular Cells	Sintered Electrodes	SD	1.6—50Ah
Monoblock Batteries	Sintered Electrodes	5 M	3—6Ah

The type number of a battery which consists of two or more cells is derived from the code for these cells, and from the number of cells used.

Example:

A 6 V battery contains 6 cells having a capacity of 600mAh. For button cells of the twin electrode type, the code is accordingly: 5/600DKZ.

For safer handling of cells and batteries by the user, the positive terminal is marked with a plus sign (+) printed or stamped on the case. Batteries with connecting leads have the polarities shown by colours based on the DIN standard.

The date of manufacture is given by a three figure code, thus:

01
January

8
1978

In former years the date of manufacture and of sale are designated by a one or two figure code. For example, the single figure code "6" gives the year of manufacture — 1976 — and the two figure code, e.g. "16" gives the six month period when the cell was made, thus this code means January — June 1976.

7.1.2 Design Groups

Sealed nickel cadmium batteries are made with two different kinds of electrode, as shown in the chart in Table 7/1, namely:

— cells with mass plate electrodes, and
— cells with sintered electrodes.

7.1.2.1 Cells with Mass Plate Electrodes

These are made as
— button cells,

The active mass is produced in powder form by an electrochemical process.

7.1.2.2 Cells with Sintered Electrodes

These are made as
— cylindrical (round) cells,
— rectangular cells, and
— Monoblock batteries.

The active mass is impregnated into a highly porous sintered grid. This grid consists of nickel powder which is produced in a special process on a continuous perforated nickel plated steel band which is placed in the middle of the grid and which acts as the carrier.

The cylindrical cell series "RSP" is a variation on the classic sintered cell model; it has a pressed negative electrode instead of a sintered plate. As distinct from the sintered type, the active mass is added as a powder directly to the grid by a rolling mill process. The grid is identical with that in the sintered electrode.

The various electrical properties and the technical applications of cells with mass plate and sintered electrodes are described in Chapters 5 and 9 respectively.

7.1.3 Constructional Details of Sealed Nickel Cadmium Batteries

7.1.3.1 Structure of Button Cells (DK — DKZ — DKO)

Button cells consist of a cup-shaped case (positive pole) closed with a lid (negative pole). Both case and lid are made of nickel plated deep drawn steel strip. The thickness of the nickel plating is about 5 µm.

The positive and negative mass electrodes consist of pressed pastilles which are enclosed in a fine mesh pure nickel wire grid. The wire thickness is less than 0.1 mm.

Between the electrodes there is a microporous separator made of non-woven plastic fibre.

A curved spring contact on the back of the negative pole exerts a pre-determined pressure on the set of plates and ensures constant contact resistance between electrode and case.

The cells are sealed by a plastic gasket round the lid. This plastic sealing ring also acts as an insulator between case and lid.

Button cells in the DKZ series, have pairs of interleaved electrodes instead of the usual single electrode pattern. For the same cell dimensions, this construction almost doubles the surface area of the electrodes. Because of the low internal resistance, this type of cell is particularly suitable for high rate discharge whilst maintaining its voltage characteristic. The electrolyte is potassium hydroxide, which is contained within the electrodes and in the separator. Fig. 7/1 shows the constructional details of a button cell in the "DK" series.

Lid
Contact Spring
Gasket
Nickel Wire Mesh
Cup
Positive Electrode
Negative Electrode
Separator
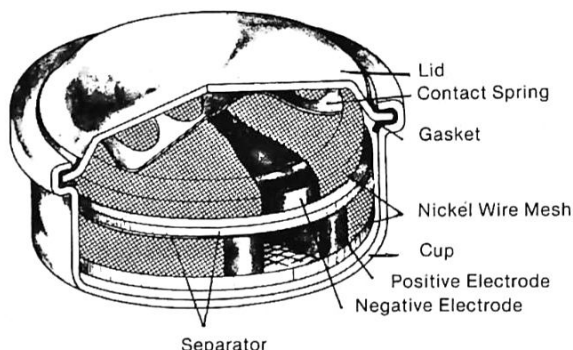
Fig. 7/1:
Schematic diagram of a button cell in the DK series

Button cells in the DK/DKZ series are made with capacities of 10 to 1000 mAh. with cell diameters of 7.65 mm to 50.3 mm, and with heights between 5.2 mm and 10.0 mm.

Departing from the usual circular shape, there is a 100 mAh capacity cell made with an oval outline. Cell type 100 DKO has an oval base, measuring 25.9 mm x 14.4 mm, with a height of 6 mm, and is not different in construction from the other cells in the DK series.

7.1.3.2 Structure of Cylindrical Mass Plate Cells (D)

Until recently, VARTA produced a range of cylindrical cells with mass plate electrodes, having cases made of deep drawn sheet steel plated with about 5 µm thick nickel. The covering lid is also nickel plated. The plastic gasket between lid and cup serves both as a seal and as an insulator between the positive lid and the negative cup. The cell is sealed by wrapping the rim of the cup over the lid.

The positive electrode consists of two parts which are connected to centre cap terminal. A welded strip connector makes contact with the lid. The active mass is pressed into the pastilles and is then enclosed in microporous pure nickel wire mesh (as in button cells).

The negative electrode is made in the shape of three curved segments, also made of pastilles, enclosed with pure nickel wire mesh, and encloses the positive electrode.

A microporous plastic mesh separator insulates the electrodes from each other. The potassium hydroxide electrolyte is held in the separator and in the electrodes. Fig. 7/2 shows the construction of a cylindrical cell with mass plate electrodes which had a capacity of 150 mAh.

The cell diameter is 12 mm and the height is 29 mm.

Cap Contact
Lid
Gasket
Positive Pole Cap
Separator
Positive Electrode
Negative Electrode
Nickel Wire Mesh
Case
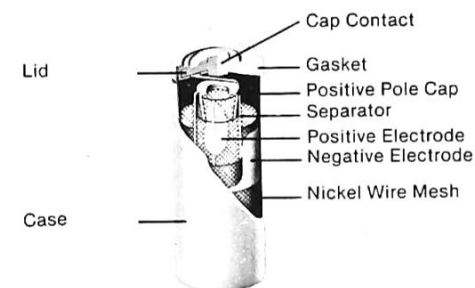
Fig. 7/2:
Schematic diagram of the construction of a sealed cylindrical cell with mass plate electrodes

7.1.3.3 Structure of Cylindrical Sintered Electrode Cells (RS)

Cylindrical cells in the RS series have electrodes made of highly porous sintered grids impregnated with the active material.

The positive and negative plates are only about 0.5—0.8 mm thick and are rolled up into a spiral. They are insulated from each other by a microporous plastic mesh separator rolled in with the plates.

The rolled electrodes are inserted into a deep drawn sheet steel can which is nickel plated to about 5 μm thickness. The current collector for the negative electrode is welded to the can, and that for the positive electrode to the lid, which is also made of nickel plated steel. Closing is effected by wrapping the edge of the can over the lid.

The circular plastic gasket serves both as a seal and to insulate the positive lid from the negative can. The potassium hydroxide electrolyte is held in the separator and in the plates.

Because RS cells are suitable for high charge and discharge currents, they are provided with a safety valve in the lid. Should excessive pressure build up in the cell through misuse, the valve will open. After the pressure has been released, the cell will re-close. Fig. 7/3 shows the construction of an RS cell, in the capacity range from 100 mAh to 7 Ah.

The smallest cell diameter is 10.5 mm, the greatest is 35.5 mm. The height is between 17.4 mm and 94 mm.
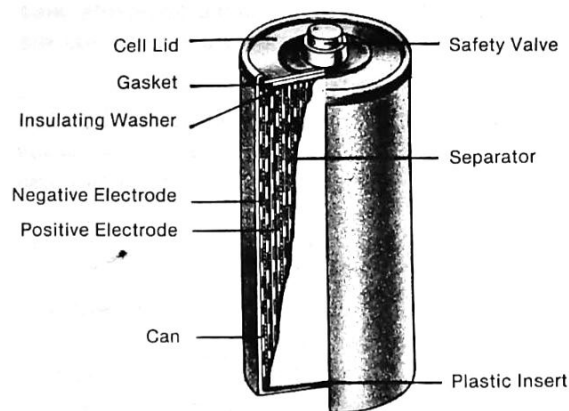
Fig. 7/3:
Schematic diagram of a sealed cylindrical sintered electrode cell

Types 180 RS, 501 RS, RSH 1.8 and RSH 4 are made in the same dimensions as dry batteries of equivalent size and are, therefore, directly interchangeable for most purposes.

Special purpose cells are designated by additional letters, e.g. H, X, T, as has been noted in section 7.1.1.

In cells of the RSH and RSX series, the internal connectors between the electrodes and the casing (can and lid) are so arranged that there is only very low resistance. The internal voltage drops are low even at high rates of discharge.

Special produced electrodes ensure that RSX cells are specially suitable for overcharging.

Series RST cells have been designed particularly for operation at high temperatures, and have a separator which is resistant to high temperatures.

The RSP series of cells are similar in construction to RS cells; only the negative electrode is different. There is a pressed electrode in place of the sintered electrode as described in section 7.1.2.2. Some electrical parameters are superior to the standard RS cells.

7.1.3.4 D Series Cells (Now Obsolete)
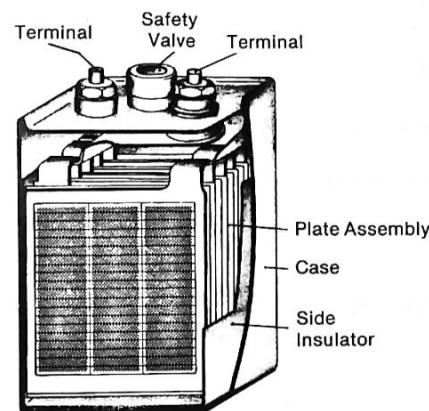
Fig. 7/4:
Schematic diagram of a sealed prismatic cell with pocket type mass electrodes

7.1.3.5 Structure of Rectangular Sintered Electrode Cells (SD)

The sintered electrodes used in these cells are 0.8 mm thick and are interleaved with separator material. This results in a very low internal resistance.

Because they are in all respects superior to mass plate cells, the SD series has replaced the D series of cells, thereby reducing the number of different types. Fig. 7/5 shows the structural details of a rectangular sintered electrode cell.

Because these cells are suitable for high rates of discharge, they are fitted with safety valves to release any pressure caused by misuse so that it will not distort the case.

Screw terminals are provided for external connections to circuits and inter-cell links.

Rectangular sintered electrode cells are made with capacities from 2.4 to 50Ah.

Terminal Safety Valve Terminal

Plate Assembly
Separator
Case

Base Insulator   Side Insulator

Fig. 7/5:
Schematic diagram of a sealed rectangular sintered electrode cell
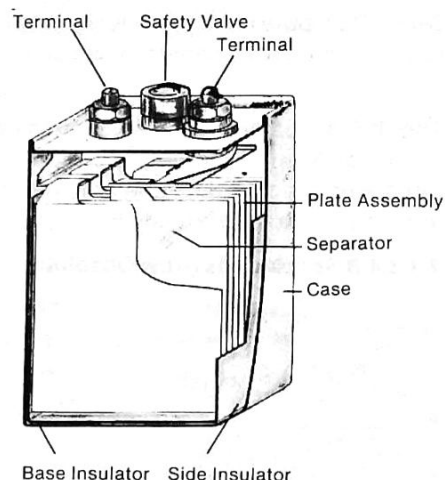
7.1.3.6 Structure of "Monoblock" Batteries (5 M)

Monoblock batteries are made with sintered electrodes similar to those in the SD series (section 7.1.3.5). Microporous non-woven plastic mesh is used in the separator between the positive and negative electrodes. The moulded plastic case with internal separators, holds five plate assemblies, interconnected by strip connectors.

The battery is covered with a plastic lid, ultrasonically welded to the case.

Both positive and negative terminals are mounted in the lid. The terminal connectors are made in such a way that they are suitable not only for "AMP" type snap-on connectors but also for soldered connections via soldering tags.

There are safety valves in the lids of all the cells to prevent damage to the plastic case by excessive internal pressure. Monoblock batteries are made in units of five cells with capacities from 3 Ah to 6 Ah.

7.1.3.7 Special Purpose Cells

Cells for special applications can be made in close collaboration with the user. Experience gained over the years during the production of standard cells forms the basis for such kinds of special product. New major developments are the outcome of proven manufacturing expertise.

Thus, for example, there is a cell specially developed from the SD series for use in space applications, type number SD 15 K. The code indicates that it is a 15 Ah cell with ceramic glands for the terminals. Both terminals are mounted on insulators in the cell cover. Both cover and can are made of stainless steel.

There is a special reinforcement of the plate assemblies to prevent damage by sinusoidal and complex vibrations, and from high g shocks. Programmed and controlled production ensures that the closest tolerances are met, and the cell balance in connection with defined charge and discharge conditions makes a safety valve unnecessary.

This totally sealed cell has a leak rate for the helium test of less than $10^{-10}\,\text{bar} \cdot \text{l} \cdot \text{s}^{-1}$.

The growth in the pocket calculator and mobile radio transceivers market has led to the development of increasingly thin equipment. To meet this demand, a flat cell is in the course of development.

This cell is made with sintered electrodes housed in a plastic case, approximately 5 mm thick and ultrasonically welded.

Besides the advantage of the flat shape, the concept of a plastic cell offers the ability of individual configurations to fit into the space available (e.g. rectangular or square) as the application demands. This means that there is greater efficiency in the use of space than when round (button or cylindrical) cells are used.

7.2 Production

7.2.1 Factories

VARTA have been making sealed alkaline batteries for more than 25 years. The product range covers the complete spectrum of present day series and types found worldwide.

Starting from the "classic" sealed alkaline battery with mass plate electrodes, the production programme very soon expanded to include the sintered electrode types. For both types of electrode, the long standing experience gained during manufacture of open alkaline batteries was of considerable help.

VARTA sealed batteries were sold under the trade name "DEAC". DEAC (Deutsche Edision Akkumulatoren Company) was a subsidiary of AFA (Akkumulatoren Fabrik AG), part of the VARTA Organization.

In the factory at Hagen the products developed and blossomed into a range of products and the foundations were laid for further expansion to meet world demand. In 1959, it was decided to establish a manufacturing base in England; and another in Singapore in 1973 to meet worldwide demands for VARTA's sealed alkaline batteries.

The state of technical development made possible by the incorporation of special components, special accessories, or selection and individual tests, to make cells available to the market which would meet specialized and, at times, very exacting demands, such as is necessary in space technology, or for more mundane apparatus such as calculators and mobile radios which needed flat batteries.

7.2.2 Raw Materials

The important raw materials used in the manufacture of sealed nickel cadmium batteries are as follows:
— nickel, in the form of anodes and as a powder
— cadmium, in the form of anodes, and as cadmium oxide
— powdered graphite
— concentrated potassium hydroxide for making up the electrolyte by adding distilled or deionized water
— sheet steel for making the cans and lids, etc.
— nickel wire mesh for holding the active mass in the electrode assembly
— plastic mesh for separators
— plastics for insulators, gaskets, and parts of the containers.

7.2.3 Manufacturing Processes

7.2.3.1 Active Masses and Electrodes

The positive and negative active mass is manufactured from the raw material in a special electrochemical plant.

For mass plate electrode cells, the nickel and cadmium compounds are prepared as fine grained powders. A nickel or cadmium salt is used for making sintered electrodes by impregnation into highly porous sintered grids.

Fig. 7/6 shows the sintering plant.

The nickel powder is incorporated onto the nickel plated steel strip by passing through a continuous furnace process. Then the positive or negative masses are deposited in the microporous nickel grid by a final impregnation precipitation process.

The strip thus produced is then cut into individual parts for the electrodes concerned.

Fig. 7/6:
Sintering Plant

For mass plate electrodes, the active material in powder form is made up into pastilles in pelleting presses, and the pastilles are then covered with the nickel gauze.

7.2.3.2 Cases

Cases, cups, lids and the electrical connectors are either punched from nickel plated sheet steel, or as deep drawn parts which are then nickel plated; injection moulded plastic parts are also used.

7.2.3.3 Cell Assembly Lines

The production of cells proceeds on assembly lines designed to match individual products. For button cell assembly, special conveyor belts are used. Fig. 7/7 gives a view of one such assembly line.
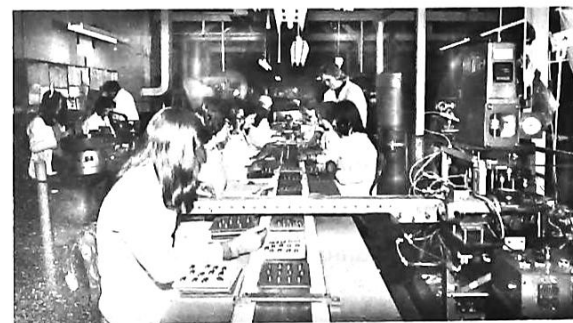
Fig. 7/7:
Button Cell Assembly Line

The flow chart shown in Fig. 7/8 gives the essential sequence of operations used in the manufacture of button cells.
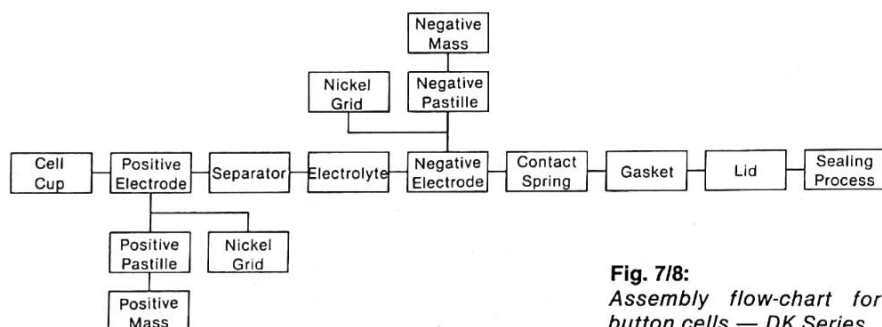
Fig. 7/8:
Assembly flow-chart for button cells — DK Series

The DKZ series of cells are assembled on interlinked conveyor belt systems.

Fig. 7/9 gives a view of cylindrical sintered RS cells being made on a conveyor belt.

Fig. 7/9:
Series RS Production Line

7.2.3.4 Commissioning and Shelf Tests
After assembly, all cells are formed during which the charge and discharge behaviour of every cell is tested.

After the electrical test, the cells are left to stand for, at least, seven days. After this period has elapsed, each cell is tested for its self discharge behaviour, and for leakage of electrolyte.

7.2.3.5 Packaging and Charge State on Delivery
After the tests mentioned in section 7.2.3.4, the cells are packed into trays of up to 100 cells, depending on size of the cells. Special packs, e.g. for hearing-aid cells, are made up to suit the needs of the customer; for example, cells type 20 DK and 60 DK are packed in pairs. All cells are in the fully charged state after manufacture. This state of charge is only reduced by the rate of self-discharge up to the time the cell is put into use.

7.2.3.6 Battery Assembly, Stacking and Finish of Individual Cells
The differences between batteries and single cells with connecting leads and/or in stack format in insulating sleeves are described in Chapter 9.

Button and cylindrical cells interconnections are made inside the stacks by spot-welding, by contact caps, or by strip connectors, the last two made of nickel plated steel. These methods of connection ensure low resistance and hence low internal voltage drop, and give mechanical strength to the stack. The cross-section of the connectors for heavy duty batteries is made suitably thicker.

Details of the external connectors on batteries can be found in Chapter 9. Connections to the end cells in battery stacks are likewise made by spot-welding to ensure low resistance.

The most common form of battery stack is enclosed in a heat shrink plastic sleeve. This is a PVC tube drawn over the cells, strengthening the stack and serving as an insulator. The plastic sleeve also used on single cells carries electrical data and instructions for the user.

When mechanically more robust batteries are required, the cells can be enclosed in sheet steel or plastic containers.

Rectangular cells are likewise encapsulated in similar plastic or steel containers. They are provided with screw terminals with which the cells are connected together. The connector strips are made of nickel plated steel of suitable cross section to suit the discharge rate.

The output connections are made of wire or solder tags.

8.1 Quality Control System

Previous descriptions will have shown that the sealed nickel cadmium battery, if it is to function properly, demands very careful manufacture and electrochemical processing of the active material. In order to meet these demands, a quality control organization was set up, which, independent of manufacturing departments, supervises every important process and stage of manufacture with specially trained personnel, working in close collaboration with production staff. These specialists, backed up by laboratory facilities, can bring a wealth of theory and expertise to the solution of possible production difficulties.

The effectiveness of quality control stems from its early participation in the design stage. From the performance specifications, the quality control criteria are established and applied to pre-production models and prototypes, and then manufacturing processes, lay-out, and instructions are evaluated. Tolerance inspections are important and critical stages in the production must be carefully controlled. Test measurement specifications and test procedures are laid down and the necessary test apparatus chosen and procured. The production staff are well briefed before the introduction of a new series of cells and made conversant by instructional courses on product characteristics and technical production problems. At the same time, the supply of the necessary materials is reviewed in respect of quality and uniformity.

The laid down test procedures are co-ordinated with the manufacturing instructions, which are based on the design drawings, specifications, necessary materials, finished products and process descriptions. The whole forms a quality control system and hence before the start of full scale production, there is close control of all the controlling factors. To ensure all these activities are co-ordinated, there is a "Technical Control" department.

One "Technical Operations Handbook" controls the whole quality control system, satisfying the stringent AQAP — 1 NATO regulations. This handbook gives descriptions of the organization, production structure and the professional competence of the staff proves that our Company is a recognized supplier of military equipment. The instructions and regulations laid down in this handbook apply to the whole of our workforce (31).

8.1.1 Product Changes

Should any components used in the finished products need to be altered, for example to improve the quality, to rationalize production or to meet some special application, then a written application is made, to set out the intention of the change. To guard against unforeseen difficulties, the application

has to be approved by all the departments concerned — design, manufacturing, quality control and sales. Not until the matter has been fully agreed will the appropriate changes be undertaken.

8.2 Quality Control During Manufacture

Because sealed batteries are made in mass production, there is an opportunity for applying statistical quality control methods.

Samples are taken on a control basis for visual inspection and dimensional checks, random sampling at specified intervals by the manufacturing personnel, along the production lines, and at all critical production stages. Because there is no better way to stimulate the urge to produce high quality workmanship than being personally responsible for the quality control of one's own products, the production staff is entrusted wherever practicable with carrying out its own checks. To guard against measuring errors, therefore, on a random sampling basis, there is a further check by one of the quality control staff.

Visual inspection is often more difficult to apply than dimensional checks because they have a certain margin of uncertainty. Collections of actual specimens with typical defects, or displays of pictures of failures have proved helpful here.

The work of the chemical, electrochemical, and metallurgy laboratories protects against falling standards of material and processing procedures. The quality of bought out parts and sub-contracted components come under the control of the laboratories. Examination methods are laid down in the instructions for measurement and analysis are based on the original specifications. If in spite of all these controls, faults occur in unacceptable number a batch has to be rejected and the cause of the trouble to be identified, followed by a decision on whether to reprocess or to scrap the material. The causes of the faulty manufacture are identified and eliminated — in complicated cases by applying mathematical methods. It should be mentioned here that in the course of its manufacture, a sealed cell undergoes more than 40 tests of a chemical , mechanical, or physical.nature.

All the findings about such failures are listed and illustrated in catalogues and all defects are collated and assembled into quality control cards so immediate remedies can be applied and the trouble eliminated. In summarized form, the details appear at approximately monthly intervals in the quality control reports. From the point of view of development and construction, these serve as sources of information for possible decisions on structural alterations, or the introduction of new designs less prone to defects, or new processes. All this comes under the responsibility of the department of "Technical Statistics".

8.2.1 Quality Control Measurements During and After Manufacture

Chemical examination of raw materials and semi-finished goods will only be mentioned and not fully described, but the importance of purity and correct composition of active materials and electrolyte cannot be overemphasized. More interesting are the electrochemical tests of the capacity of the active mass and of complete electrodes, which must fulfill minimum requirements per unit weight or area.

Because the active mass and complete electrodes are, during the course of manufacture, subjected to further processes and changes, the performance of the finished cells and batteries has to be established during the final operations on the production line. In addition, there are daily product tests of random samples where batches of the day's production are evaluated depending on type and application. This includes capacity tests, measuring of end-of-discharge voltage, cell balance, self discharge and internal resistance.

The tests serve mainly for product performance evaluation, and enable a first decision whether the goods can be released for sale.

Beyond that, they provide information on the cell characteristics which are critical to the end user. Of primary importance is the end-of-charge voltage, and also details of internal resistance, gas recombination, electrolyte retention and the electrical contacts.

The self-discharge can be checked by measuring the off-load voltage. Because self-discharge can have mechanical as well as chemical origins, its temperature coefficient is of interest.

The ratio of the positive and negative electrode capacities and their balance are important parameters controlling the gas pressure within the cell. The capacity distribution in a sealed cell in terms of useful capacity, charge and discharge reserves is summed up in the term cell balance. Adjustment of cell balance determines the type and amount of on-charge gassing. It is evident that continuous hydrogen evolution can be controlled by means of a vent, but the loss of hydrogen causes further changes in cell balance, loss of electrolyte and more particularly drying out. Hence cell balance is so designed from the start that evolution of hydrogen will not occur, even during overcharge.

8.2.2 Examples of Post-Production Electrical Tests

The cell capacity is usually evaluated at a discharge rate of 0.2 CA down to 1.0 V. The continuously improved high discharge current performance has opened up new ranges of application. This has resulted in tighter quality control and new methods of testing.

Thus cells with a very fast current rise-time followed by exponential decay were developed for photoflash units. The measurement of the extractable

current is difficult because the current/time characteristic is itself falling with each reading as the cell voltage decreases. In collaboration with various battery users, VARTA has been able to simplify this problem by checking the peak current performance with a constant current discharge test at, for example, 2 CA. To check peak current performance, there is a high current short term discharge via a limiting resistor of 120 mOhms, DKZ cells, for example, can deliver currents up to $20C_5A$ for 2 seconds.

In special cases, as with cells for mobile radio sets, the whole sequence of the transmitter and receiver currents can be followed. Here also it has proved possible to relate performance under these conditions with the capacity characteristics at constant current discharge.

Customer-specified discharge rates are checked so far as is necessary as standardized discharge tests in the manufacturing plant. These tests are backed up with additional random sampling when cells are taken for separate measurement by quality control staff in sufficient quantities to ensure statistical accuracy.

The working life of any sealed cell is of considerable interest to the user. IEC 285-1 specification requires a useful life of 392 cycles from RS cells, in tests of 28 cycles at a time. Each set of tests comprises of 27 charge and discharge cycles with a capacity test on the 28th cycle. The cell is regarded as having passed the test when the 392nd cycle achieves more than 60% of the rated capacity. VARTA RS cells more than double this number of cycles, i.e. greater than 784 cycles. The VARTA factory specification states 784 minimum.

IEC 509 is the corresponding standard for button cells. Developments in recent years have made more than 1000 cycles possible, satisfying the IEC standard by almost a factor of three.

8.3 Symptoms of Defects

The statistical distribution of capacity values, especially for small cells, poses an important problem. In the manufacture of cells with a single pair of electrodes, it is obvious that it is not possible to connect up groups of electrodes in parallel with each other in order to compare electrode capacity as is possible with large "open" cells. Hence, statistical averaging of the various individual electrode capacities is achieved. In the manufacture of an RS cell, there are more than 30 factors that affect performance, so there is a possibility of an undesirable spread in the characteristic capacity. There are several ways of controlling this state of affairs, which is particularly important when related to deep discharge. There are sorting processes available which can match battery plates of different capacities so that a better capacity distribution can be achieved. It is possible to produce the active mass in such a way that over-discharge does not affect their performance. This is the method chosen for button cells.

Occasionally a white crystalline deposit forms on sealed cells near the sealing ring after a period of service or storage. This is caused by traces of electrolyte, which, as research has shown, involve only a few milligrams of electrolyte, or less than one part in a thousand of the cell's electrolyte content. Amounts of crystalline deposit in this order obviously are not indications of cell malfunction. The crystals are of potassium carbonate formed by interaction of electrolyte with the carbon dioxide in the air; they are not caustic and can be easily washed off. The reason for this penetration of the seal by the electrolyte is that aqueous solutions of potassium hydroxide have extraordinary powers of creepage — a fact not generally known. This liquid can work its way through seals which are otherwise thoroughly sealed.

When these cells are tested in the laboratory by placing them in oil under high vacuum, it is not possible to detect even a single bubble of escaping gas, in contrast to cells with faulty seals which reveal their defect by emitting streams of bubbles.

In order to be able to segregate imperfectly sealed cells, all cells are stored after production for a period in excess of seven days, and inspected for escape of electrolyte; in special cases, the period may even be 14 days. This period also allows any internal short circuits to show up by a fall in the off-load voltage and these cells can be rejected.

9. Application Techniques

9.1. Different Cell and Battery Types

9.1.1 Introduction

Due to their outstanding performance, nickel cadmium batteries are used for a wide range of applications. Their important advantages include:
— long life; in cyclic operation, at their rated current up to 1000 cycles or more; on trickle charge, a life of greater than 6 years,
— uniform voltage level during discharge,
— simple and economical charging, also fast charging,
— unaffected by over-discharge, polarity reversal at the rated current and overcharging,
— usable at temperatures down to —45 °C,
— very robust,
— low self-discharge, particularly with mass plate cells,
— can be installed in any working position because the electrolyte is retained in the electrodes and separators,
— almost unlimited storage, at any state of charge,
— completely maintenance free over the working life,
— very wide range of cell sizes available.

Fig. 9/1:
Button cell, cylindrical cell and rectangular cell

These properties ensure that the correct type of cell can be tailored to the consumer's application.

The construction of sealed nickel cadmium batteries has been described in Chapter 7. They are basically divided into:
— sealed cells with mass plate electrodes,
— sealed cells with sintered electrodes.
    Further, there are three different forms (Fig. 9/1) as follows:
— button cells,
— cylindrical cells,
— rectangular cells.

Fig. 9/2:
Comparison of size: matchstick and the smallest nickel cadmium cell

9.1.2 Nickel Cadmium Batteries with Mass Plate Electrodes
Cells with mass plate electrodes are specially suited for low rate to medium rate of discharge, i.e. from discharge times of the order of months on µA. loads to fully discharged in 30 to 60 minutes. The particular advantage of these cells is their very low self-discharge compared with other kinds of battery, especially at temperatures of 20 °C and below (Figs. 5/75 and 5/76), a property which is prerequisite for long life at low discharge rates, e. g. volatile electronic memory storage systems. Apparatus that is fitted with these cells, e.g. a photoflash unit, is ready for instant use without charging even after months of storage.

In addition, cells with mass plate electrodes need not be fitted with safety vents, which are needed with all other types of cell, because they can withstand polarity reversal and can even withstand several hours charging in the wrong direction without being damaged.

Omission of the safety vent allows cells to be made in very small sizes. The smallest mass plate electrode cell is hardly larger than a pea and has a capacity of 10mAh (Fig. 9/2).

Complete hermetic sealing of cells is vitally important when for some applications it is necessary to avoid emission of gasses produced during overcharge, or of the electrolyte.

VARTA makes two different kinds of mass plate cell:
— Button cells in the DK series.

Capacities from 10mAh to 1000mAh with various connectors in units of 1 to 10 cells (see section 9.1.7 and 9.1.8 — Battery types and connectors). Cell type 10 DK is only available as a single cell, due to its very small size. Cell type 100 DKO, with an oval outline, is a button cell in common use.
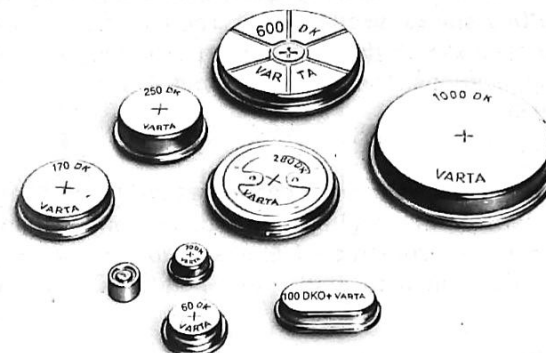

Fig. 9/3:
Series DK Cells

— Button cells with twin electrodes, series DKZ
Capacities from 225mAh to 1000mAh Series DKZ cells can supply heavier currents than the DK series because of their low internal resistance, and they can also be used down to temperatures of —20 °C (Fig. 9/4).
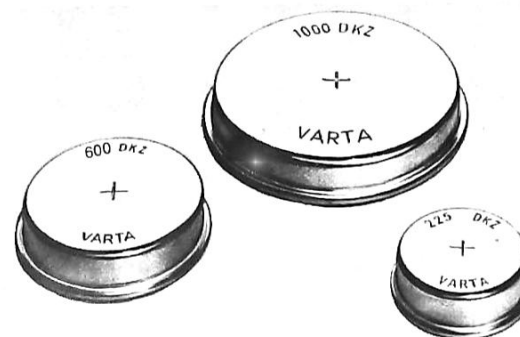

Fig. 9/4:
Series DKZ cells

9.1.3 Nickel Cadmium Batteries with Sintered Electrodes

Cells made with sintered electrodes are particularly suited for high rate discharge, also for use at low temperatures, down to —45 °C. Special types can be discharged continuously at rates up to $10C_5A$, short term loads up to $40C_5A$, and can also withstand considerable overcharging over long periods of time (Table 9/1).

VARTA makes a range of cells of this type, as follows:

— cylindrical (round) cells in Series RS

Capacities from 100mAh to 7Ah, with self-sealing safety valves, available as single cells or in various battery stacks (section 9.1.9). The modified series RSH (high current performance) and RSX (for high current overcharge) have been produced for special applications. The series RSP and RST have been recently developed (section 5.5).

— Rectangular cells, Series SD

Capacities 2.4Ah to 50Ah in which range cells of capacities 25Ah and 50Ah are only sold as complete batteries with charging units and monitoring equipment. Sealed rectangular cells are constructed similarly to open nickel cadmium batteries; their size is suited to stationary operations, e.g. for standby power supplies.

Rectangular cells in the SD series are usable at temperatures down to —30 °C.
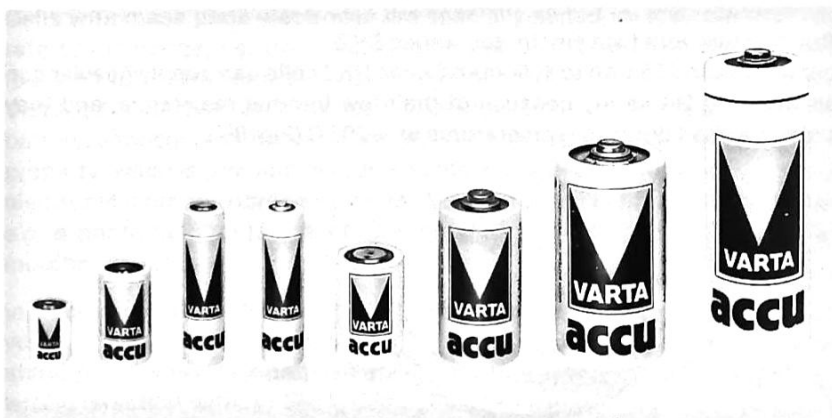
Fig. 9/5:
Series RS Cells

— Monoblock batteries, Series 5 M

Capacities 3Ah and 6Ah, in two models enclosed in plastic cases. Monoblock batteries in the 5 M series can be used down to temperatures of —30 °C.

Table 9/1:
Average values of maximum loads, discharge voltages and extractable capacities for the different battery series

Series	Constant Load Maximum Recommended CA	Constant Load Extractable Capacity %C	Discharge Voltage Mean V	Discharge Voltage Final V	Short Term Load Recommended CA	Short Term Load Period Of Load Min.	Short Term Load Recommended Mean V	Short Term Load Recommended Final V	Pulse-Discharge Recommended CA	Pulse-Discharge Recommended Discharge Period Sec.	Pulse-Discharge Recommended Minimum Discharge Voltage V
DK	1CA	60% in Approx 36min.	1.10	0.9	2CA	8-10	1.05	0.9	4CA	2	0.75
DKZ	2CA	70% in Approx 21min.	1.15	0.9	3.5CA	8-10	1.05	0.9	8CA	2	0.75
RS	6CA Up to 1Ah	75% in Approx 7.5min.	1.15	0.9	10CA	2-3	1.1	0.9	20CA	2	0.75
RS	4CA Up to 2Ah	75% in Approx 11min.	1.15	0.9	8CA	2-3	1.0	0.9	16CA	2	0.75
RSH	10CA Up to 1.8Ah	70% in Approx 4.5min	1.15	0.9	16CA	2-3	1.1	0.9	40CA	2	0.75
RSH	6CA Above 2Ah	80% in Approx 8min.	1.15	0.9	12CA	2-3	1.1	0.9	25CA	2	0.75
RSX	10CA	80% in Approx 5min.	1.15	0.9	16CA	2-3	1.1	0.9	40CA	2	0,75
RSX	6CA	90% in Approx 9min	1.15	0.9	12CA	2-3	1.1	0.9	25CA	2	0.75
SD	4CA	60% in Approx 9min	1.15	0.9	8CA	2-3	1.1	0.9	10CA	2	0.75
Mono-block	1CA	90% in Approx 54min.	1.15	0.9	2CA	8-10	1.1	0.9	40CA	2	0.75

Fig. 9/6:
Monoblock battery 5 M 3,
5 cells in a plastic case

This series has five cells in a single plastic case and, therefore, saves space and weight. These 6V units can be joined in series, and their application ranges from use in video and sound reproducing equipment to static operation.

9.1.4 Guidelines for Design of Batteries

Table 9/1 lists for the different series the average values of the recommended loads, end-of-discharge voltages and the extractable capacities. There are also Tables 9/2, for overall temperature specifications for charge, discharge and storage, and 9/6 for the various charging methods. This information is sufficient for an initial design stage and more detailed data is available in leaflets each of which is specific for the cell type and will enable the choice of the most suitable type for the application to be made. Detailed information which is of importance for circuit design is included under **Electrical Performance** (discharge — sections 5.1 and 5.4), **Charge and Overcharge** (sections 5.2, 5.4.8 and 9.3), **Self-Discharge** (section 5.6.2), **Stored Energy** (section 5.4.7), **Temperature Behaviour** (sections 5.3, 5.4.8 and 5.5.3), **Useful Life** (section 5.6.3) and **Environmental Factors** (sections 6.2.4 and 6.2.5). Before making final decisions, reference should be made to the detailed technical specifications which are available for each battery type.

9.1.5 Button Cell Battery Types

Batteries consist of several cells connected together, in order to achieve the required voltage (nominal voltage 1.2V per cell). For mobile equipment, mostly 2 to 10 cells are used in stacks, stationary installations can require higher voltages.

Batteries are mainly connected end-to-end and sleeved, and are also enclosed in plastic cassettes.

The most commonly used battery type consists of a series of button cells in a plastic sleeve. These are assembled from individual cells in stack formats with contact cups, joined end-to-end in series, spot-welded and enclosed in a heat shrink PVC sleeve. This insulating sleeve also provides the mechanical strength of the stack and is tested to 20 kV/mm (Fig. 9/7).

It is technically possible to make up stacks of cells with intermediate voltage tappings. Since there may arise some charging problems it is recommended to use individual batteries for the devised intermediate voltages. Stacks can also be made up in pairs in a plastic sleeve (Fig. 9/8).

Fig. 9/7:
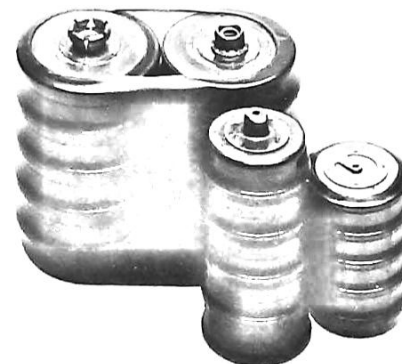*Button cell battery 4/600 DKZ in plastic sleeve, with spot welded strip connectors*

Fig. 9/8:
Button cell stacks in plastic sleeving with press stud contacts, contact cap and spot welded solder tags

Table 9/2:
Temperature Range for the Different Series for Charge, Discharge and Storage

Series	Charge		Discharge		Storage		Remarks
	Recommended	Permitted	Recommended	Permitted	Recommended	Permitted	
DK	$10 \div 35\,°C$	$0 \div 45\,°C$	$20 \div 45\,°C$	$-30 \div 50\,°C$	$0 \div 45\,°C$	$-40 \div 50\,°C$	
			Note: At temperatures below 0 °C. max. discharge current $I_{max} = 0.5C_{10}A$ 2. Permitted max. 24h up to 60 °C		Note: Permitted max. 24h up to 60 °C		
DKZ	$10 \div 35\,°C$	$0 \div 45\,°C$	$20 \div 45\,°C$	$-45 \div 50\,°C$	$0 \div 45\,°C$	$-40 \div 50\,°C$	Mass Plate Electrode Cells
			Note: At temperatures below 0 °C. max. discharge current $I_{max} = 1C_5A$ 2. Permitted max. 24h up to 60 °C		Note: Permitted max. 24h up to 60 °C		
RS, RSH, RSX	$10 \div 35\,°C$	$-20 \div 50\,°C$	$0 \div 45\,°C$	$20 \div 50\,°C$	$0 \div 45\,°C$	$-45 \div 50\,°C$	
	Note: At temperatures below 0 °C. charging current limited to 0.03 to $0.05C_5A$ and charge voltage to 1.55V per cell.		Note: Permitted max. 24h up to 60 °C		Note: Permitted max. 24h up to 60 °C		
SD, 5 M	$10 \div 35\,°C$	$-20 \div 50\,°C$	$0 \div 45\,°C$	$20 \div 50\,°C$	$0 \div 45\,°C$	$-30 \div 50\,°C$	Sintered Electrode Cells
	Note: At temperatures below 0 °C charging current limited to 0.003 to $0.05C_5A$ and charge voltage to 1.55V per cell.		Note: Permitted max. 24h up to 60 °C		Note: Permitted max. 24h up to 60 °C		

Injection moulded plastic containers in the form of cassettes of rectangular, oval or round sections are mechanically stronger than plastic sleeving. Stacks of cells are preferably assembled in these thin containers, mostly without the shrunk-on sleeve for the sake of better heat dissipation. The best known button cell battery in a plastic container is type TR 7/8. This incorporates 7 type 100 DKO cells (Fig. 9/9).

If batteries are changed frequently, e.g. in radio communication sets, it is advantageous to use the moulded plastic cassette type. These are made by ultrasonic welding of plastic sheeting after the cells have been formed into stacks.

Fig. 9/9:
Button cell batteries in plastic containers (TR 7/8, 4/100 DKO)
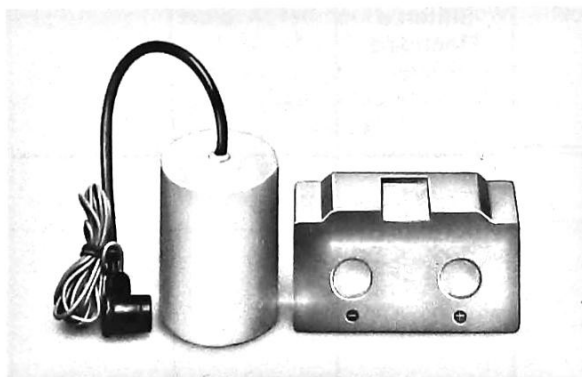

Fig. 9/10:
Button cell batteries in plastic cassettes, 4/600 DKZ and 8/280 DK

Stacks of cells in sleeving or cassettes are made up to a nominal voltage of 12V, i.e. with 10 cells. The illustrations show the different types of construction available. It is always best to keep to already available battery designs; the design and tooling for a new plastic container involves high cost and is, therefore, only to be contemplated for large numbers of units.

9.1.6 Connectors for button Cells and Button Cell Batteries
The connectors for the positive and negative terminals should be of different shapes, so far as is practicable. Button cells have the following polarity:
— cell cap ≙ positive (+)
— cell lid ≙ negative (−)
The various types of contacts available are used not only for single cells but for stacks of cells. The examples which follow show the most commonly used connectors. For battery stacks with large numbers of cells, other types of press or plug contacts may be used.

For the simplest type of connection, the contact surfaces of a cell or the end cells in a stack, are used to make pressure contact with a spring. It should be noted that it is not possible to solder directly to cells, so only pressure connections can be made. Spring contacts should be nickel plated; a contact pressure $\leq 5N/cm^2$ is satisfactory.

Strip connectors (Fig. 9/11) are made from nickel plated sheet steel. They serve both as output connectors for batteries and as connectors between adjacent cells in the battery stack. When used for output leads, the strip connectors can be provided with holes for wires to be attached, similar to those on solder tags (conductivity 7.38 Sm per mm^2).

The free end of the connector is available, not less than 5mm, nor more than 40mm, with intermediate steps of 5mm. The size chosen should be specified with a tolerance of ± 1 mm.

Example:
Specified free end, hence dimensions from perimeter of cell or battery connector 15mm or 25mm. With a manufacturing tolerance of ± 1mm, the connector overlap will be between 14 and 16mm, and 24 and 26mm respectively.
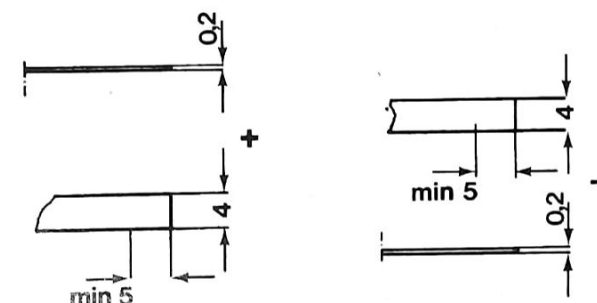

Fig. 9/11:
Strip connectors

Circular Connectors with Single Solder Tag (Fig. 9/12)

The same pattern is used for both negative and positive terminals for all cells up to 600mAh.

Tag thickness 0.15mm.

Solder tag hole takes maximum wire cross section $1.5mm^2$ (conductivity 7.38 Sm per mm^2).
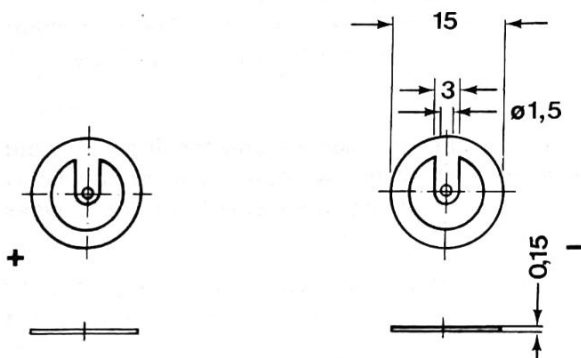
Fig. 9/12:
Circular connector with single solder tag

Circular Connectors with Two Solder Tags (Fig. 9/13)

The same pattern is used for both negative and positive terminals for all cell types with 600mAh and above.

Tag thickness 0.15mm.

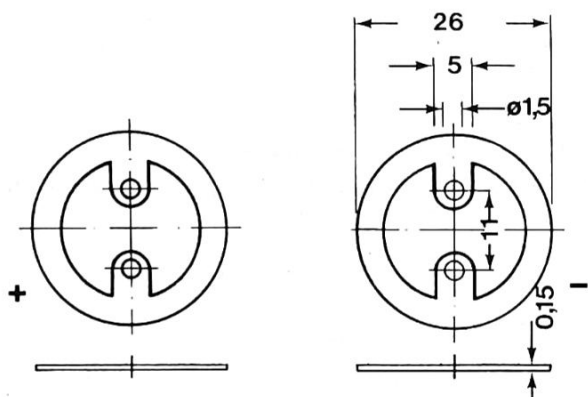Solder tag holes take maximum wire cross section $1.5mm^2$ (conductivity 7.38 Sm per mm^2).

Fig. 9/13:
Circular connector with two solder tags

Contact Stud for Positive Terminal, Contact Plate for Negative Terminal (Fig. 9/14)

The pattern is similar to that used for dry cells. Spring contacts mounted in the equipment are used for contact with the batteries; a spring pressure

$5N/cm^2$ is recommended. Pure nickel is suitable for the contacts in the appliance, but nickel plated steel or stainless steel can also be recommended.
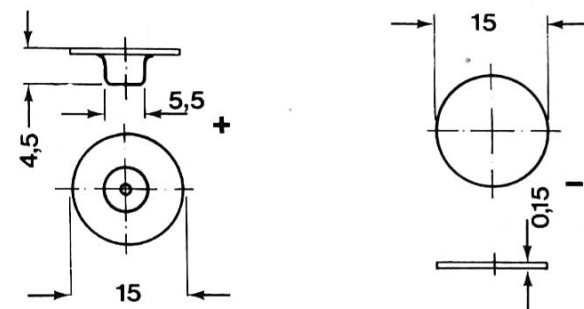
Fig. 9/14:
Contact plate for the negative terminal contact stud at the positive terminal

Press-Stud Contacts per Specification DUF 3 1/4 (Fig. 9/15)

Male contact for positive terminal, female connector for negative terminal. The standard female connector to hold the stud is made to DUF 3 1/4 design specification for all cells up to and including 600mAh.

Identical pattern press-stud and socket are used in the reverse sense for the external connectors.

Press-stud contacts can also be used in pairs, with a separating distance of 12.7mm between them, for which matching external connectors can also be made.

Fig. 9/15:
Press-stud contacts to specification DUF 3 1/4

Large Press-Stud Contacts to Specification DUF 4 (Fig. 9/16)

Stud for positive terminal, female socket for negative terminal. Press-stud contacts per DUF 4 are used on all cells including and above 600mAh.

Fig. 9/16:
Press-stud Contacts DUF 4

Spade terminals (Fig. 9/17) are made for batteries which are to be mounted on P.C. boards with single prong for the negative, and double prong for the positive terminal.

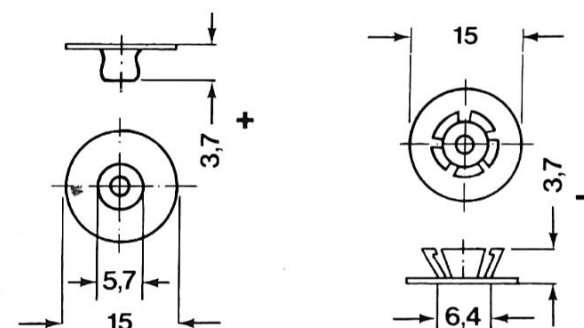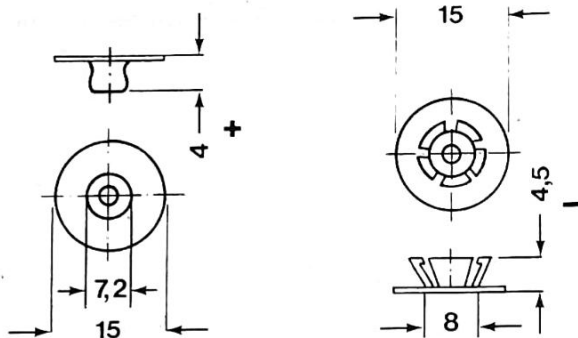Batteries with these connectors can be soldered directly into printed circuit boards, remembering that when solder bath techniques are used, cycle times should be restricted or discharged batteries should be used (connector conductivity 7.38 Sm per mm^2).
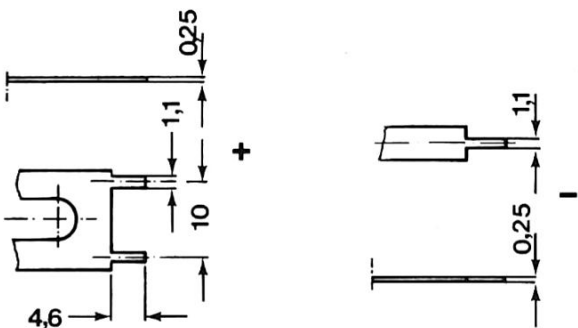
Fig. 9/17:
Spade terminals for use with printed circuits

9.1.7 Cylindrical Cell Batteries

The usual form is a stack of cells end-to-end in contact with each other and encased in a plastic sleeve (Fig. 9/18), or mounted in light plastic clips or in cassettes.
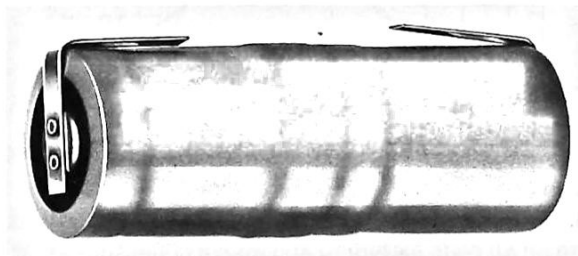
Fig. 9/18:
Battery of two round cells, type 2/100 RS with solder strip connectors

Because batteries are generally fixed inside the equipment, the most common type is a stack inside a plastic sleeve.

To make these battery stacks, the individual cells with contact cups are placed in series, spot-welded and covered with the plastic sleeve (2 to a maximum of 6 cells according to type of cell). These stacks can be assembled side by side and held in another sleeve, or glued together, and then with strip interconnections made up into larger batteries.

In another type, the individual cells are assembled in the form of a triangle, or arranged in several rows with interconnecting strips to make up a battery (Fig. 9/19) to give the desired voltage. After assembly, the cells can be glued together, or covered in a plastic sleeve.

The type described above make up handy battery units which can be provided with a wide variety of terminal connectors.

Fig. 9/19:
Batteries 5/RS 1 and 10/452 RS. Individual cells in sleeves, glued together and interconnected with strip connectors. Strip connectors used for the output terminals

When cells are assembled side by side in groups of between 2 and 10 cells, nine ways can be recommended for making up battery groups (Fig. 9/20).

Fig. 9/20:
Schematic diagram of cell arrangement for cylindrical cells made up into batteries of between 2 and 10 cells
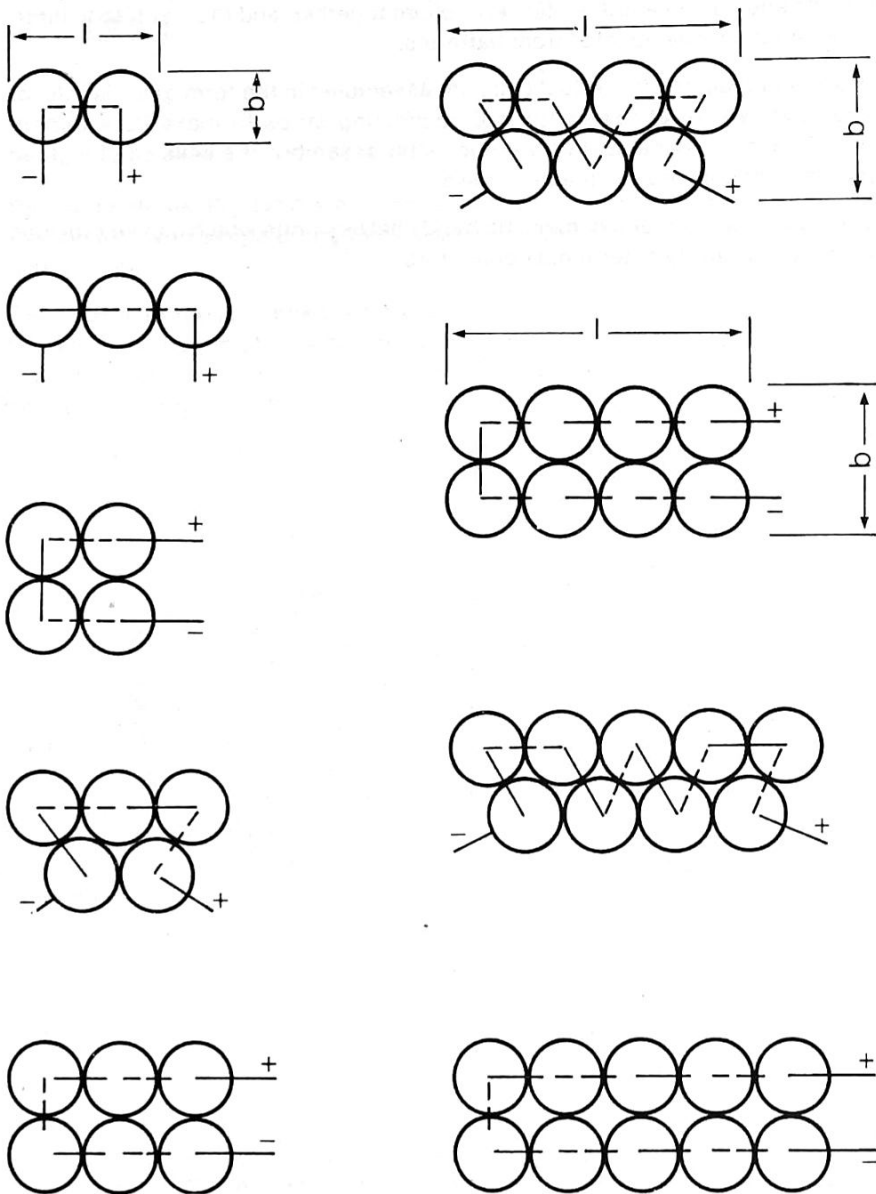
When it is necessary to increase the mechanical strength of these batteries, additional plastic covers and bases can be used, as shown in Figs. 9/21 and 9/22.

As already mentioned, cells can also be mounted in plastic cassettes or cases; this design is advisable if alternate batteries are used (Fig. 9/23).
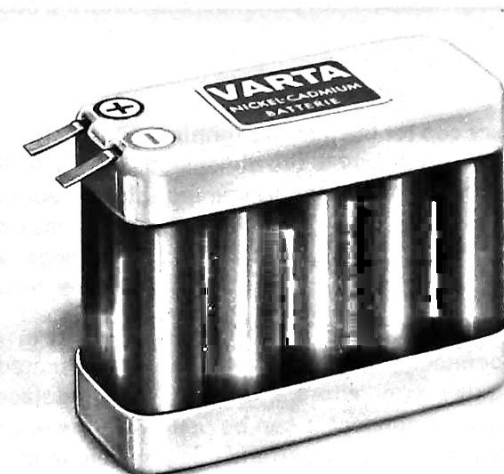
Fig. 9/21:
Battery 10/500 RS with plastic end caps, individual cells insulated with sleeving. External connector strips shown but non-reversible stud and socket contacts are also possible
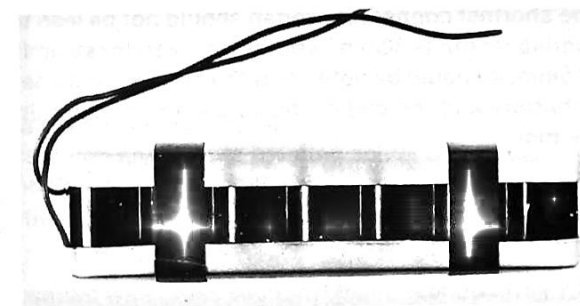
Fig. 9/22:
Battery 7/RSH 1.2 with plastic end caps, specially engineered for battery-powered model aircraft. External connection via flying leads and sockets

Fig. 9/23:
Battery 10/RS 1 encapsulated in a plastic cassette, with press-stud contacts (not shown)

9.1.8 Connectors for Cylindrical Cells and Batteries

Individual cells are made with flat contacts for the purpose of assembly into battery stacks, but they can also be sleeved and provided with connecting leads for building directly into equipment. Cells have the following polarities
— Lid ≙ positive terminal (+)
— Case ≙ negative terminal (—)
For single cells, or for batteries, the following connectors are available:

Contact cap for the positive terminal (Fig. 9/24)
This type conforms to the dimensions of DIN 40 766, the same as that for dry batteries. Batteries are connected into the equipment by means of springs mounted in the battery housing for which a maximum pressure of 5 N/cm^2 is recommended. Springs are also used for negative connectors. Pure nickel, nickel plated steel and stainless steel are recommended for contacts in equipment.

Strip connectors (Fig. 9/25) consist of nickel plated sheet steel and serve both as terminal connectors and for joining up adjacent cells in battery stacks. This type of connector can be used with the entire RS series (with flat lids). Besides the standard pattern, it is possible to make a change in the position and length of the strip when large numbers of units are involved.

The shortest connector overlap should not be less than 10mm. The maximum overlap length is 30mm; lengths between these limits can be chosen in steps of 5mm. It should be noted that the distance between the perimeter of the cell or battery and the end of the connector is maintained to a tolerance of T = 1± mm.
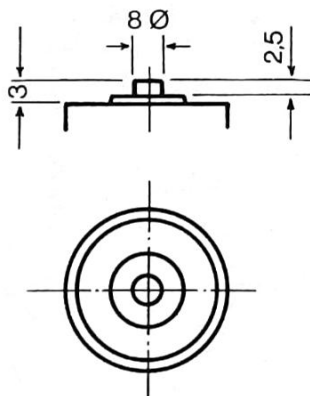
Fig. 9/24: Contact cap

Example:
Specified overlap 15mm. With a manufacturing tolerance of ± 1mm, the connector overlap lies between 14mm and 16mm.

When a strip connector is used for the terminal of a battery, it can be provided with a hole for attaching a wire (conductivity 7.38 Sm per mm^2). Cell connectors of 8mm x 0.2mm are used in RSH batteries for high discharge rates.
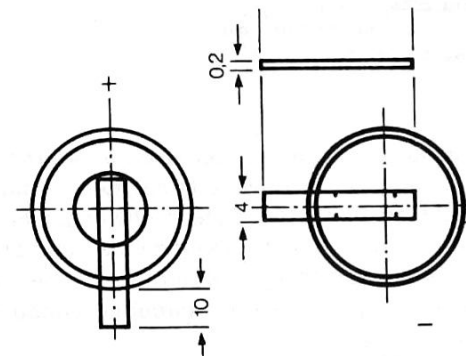
Fig. 9/25: Strip connector

Circular connector with single solder tag (Fig. 9/26).
A welded circular connector with an outward pointing solder tag for the positive terminal, inward pointing tag for the negative terminal, used for all cells and batteries with capacities from 750mAh to 1.8Ah.
Tag thickness: 0,2mm.

Solder tag hole takes maximum wire cross section 1.5mm^2 (conductivity 7.38 Sm per mm^2).
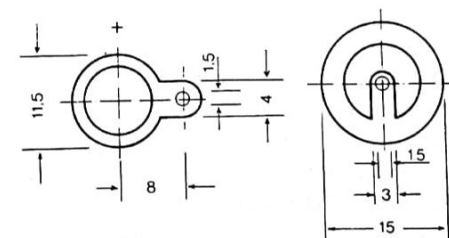
Fig. 9/26:
Circular connector with single solder tag

Circular connector with two solder tags (Fig. 9/27).
C-shaped ring for the positive terminal, complete ring for the negative terminal, used for all cells and batteries with capacities of 2Ah and above. Solder tag hole takes maximum wire cross section 1.5mm^2 (conductivity 7.38 Sm per mm^2).
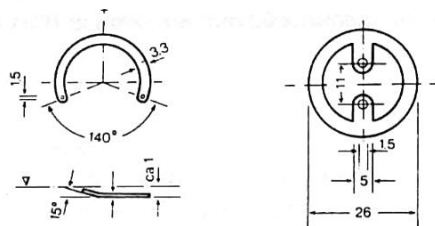
Fig. 9/27:
Circular connector with two solder tags

Spade terminals for cells used in printed circuit boards (Fig. 9/28) have one spade for the positive terminal, two for the negative; for cells up to 17mm diameter also a single spade for the negative terminal. Batteries with this type of connector can be soldered directly into printed circuits. It should be remembered that discharged batteries must be used for solder bath soldering, otherwise the cell will be short-circuited (conductivity 7.38 Sm per mm^2).

Fig. 9/28:
Spade solder tags

As used for cell types
100 RS to 500 RS

As used for cell types
750 RS to RS 7

9.1.9 Rectangular Cells, Battery Stacks and Connectors

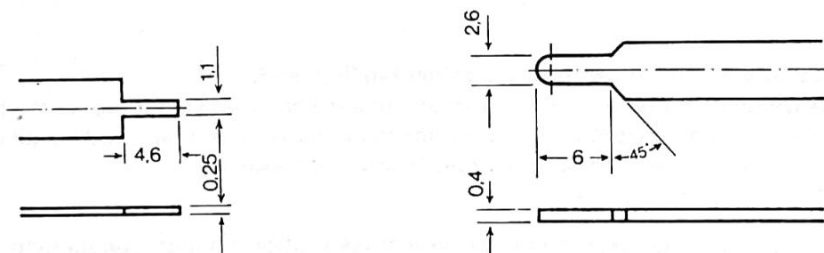Rectangular cells have two screw terminals fixed into the lid. The positive terminal is connected directly to the lid; the negative is insulated from the lid by a gland. Screw terminals have the following threads:
Cell type SD 1.6 to SD 7 = M 4
Cell type SD 15   = M 10

Sheet steel cases, also plastic cases are used in increasing numbers (Fig. 9/29), to house battery assemblies. Plastic separators are used for insulation between cells, separating them by 3mm. There is also an additional distance of 1.5mm from the bottom of these cases to the cells. The distances must be maintained in order to assist cell cooling.

For small numbers of cells, specifically for low rate discharge where space is limited a minimum distance of 0.5mm between cells is permissible.

Solder tag contacts or wire leads of various types can also be fitted to batteries. It is also possible to fit these cells singly into equipment, or put them into stationary equipment first and then connect them up to form batteries.

Fig. 9/29:
Battery 3/SD 2.6 consisting of three rectangular cells with sinter electrodes in a plastic case

9.1.10 Encapsulated Batteries

For some fields of application, e.g. for gas leak monitors, batteries can be encased to protect them from the environment, or to prevent an explosion. Button cell batteries are best for these applications because they require no safety vents. Before encapsulation, they are overcharged for a few hours at the rated current I_{10} in order to take into account any breathing effects.

It is best to use cold-setting two compoment liquid epoxy resins for the encapsulating material. Resins with a high degree of flexibility when cured, are chosen because they can tolerate pressure changes. Thermal setting resins set at temperatures greater than 60 °C, must be avoided.

When cells with safety vents, such as cylindrical sintered cells, are to be encapsulated then a vent has to be provided. This is most easily done by plac-

ing a Perlon thread by each cell, which after curing can be pulled out through the resin. However, it is best not to use this type of cell due to the vent whenever the application involves explosion or environmental hazards. Completely encapsulated cells with safety vents, but without vents through the resin, are obtainable for these purposes and have flexible rubber expansion chambers built into the case.

Flexible insulated cables are suitable for the connectors, connected to the cell terminals before encapsulation and held in position whilst the resin is poured in (EN Standard for encapsulation is in the course of preparation).

9.1.11 Interchange with Primary Batteries
A number of sealed nickel cadmium batteries have the same external dimensions as dry batteries (primary batteries). These sealed batteries are, in most cases, interchangeable with dry batteries, and provide very economical substitutes in many applications (Table 9/3).

Table 9/3:
Physically Interchangeable Nickel Cadmium Batteries and Dry Batteries

Type of Construction	VARTA Ni-Cd Cells or Batteries	VARTA Dry Batteries (Alkaline)	VARTA Dry Batteries (Manganese Dioxide)
Button Cell	10 DK	4012 4013	—
Button Cell	20 DK	4076 4675 4676 4677	—
Button Cell	60 DK	4625 4626 4627	246
Transistor Battery	TR 7/8	—	2022, 3022
Lady Cell	151 RS	4001 4401	245
Micro Cell	180 RS	4003	239
Mignon Cell	501 RS	4006	1006, 2006, 3006
Baby Cell	RSH 1.8	4014	1014, 2014, 3014
Mono Cell	RSH 4	4020	1020, 2020, 3020, 222

Although dry batteries have a nominal voltage of about 1.5V per cell, the average final voltage on discharge is rather lower than that of sealed cells because these batteries in general and nickel cadmium batteries in particular have very stable voltage characteristics during discharge. With dry batteries, on the other hand, the voltage falls immediately, especially with the ordinary types of dry cell.

When dry batteries are replaced by sealed batteries, single cells are used, with the exception of the 9V battery (TR 7/8). Simple to handle charging equipment is available for all types of cell. A detailed table of the cells involved (10mAh to 4Ah) and their charging units can be found in the Appendix (Table 14/10).

9.2 Range of Application and Use

9.2.1 Applications
A survey of all the applications shows that a wealth of experience is available for the benefit of the equipment designer. Knowledge of the range of applications forms the basis of a preliminary selection of the types and sizes of batteries which can be considered for possible use.

For the purposes of application, batteries can be conveniently divided into the following groups:
— batteries for portable equipment,
— batteries for stationary use.
Table 9/4 summarizes the most important fields of application.

The first application of nickel cadmium batteries was in cordless appliances, e.g. torches, measuring instruments, electronic photoflash units and hearing aids.
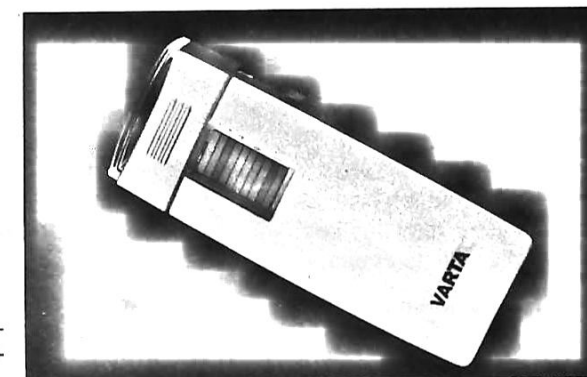
Fig. 9/30:
Hand-lamp with rechargeable DK series nickel cadmium batteries
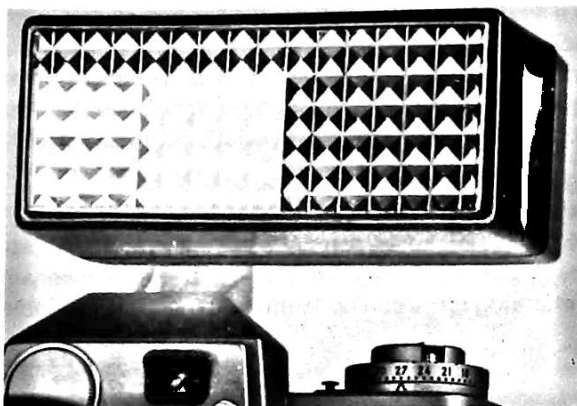
Fig. 9/31:
Electronic photoflash containing DKZ series battery

Fig. 9/32:
Electronic pocket calculators and their batteries

Fig. 9/33:
Remote control applications (DKZ series) and power for driving models (RSH series)

Fig. 9/34: *Portable radio communication set using DK, DKZ or RS batteries*

The range of these applications has become larger in recent years and the end is not yet in sight. In particular, there have been vast strides in the electronics field which have resulted in the position that the loads taken by many electrical devices has been greatly reduced so that there is an ever widening circle of cordless appliances powered by batteries.

Recent developments in nickel cadmium batteries have brought about new applications, such as powered model aircraft (series RSH), and moped flasher lights and lighting (series RSX).

Table 9/4: *Applications*

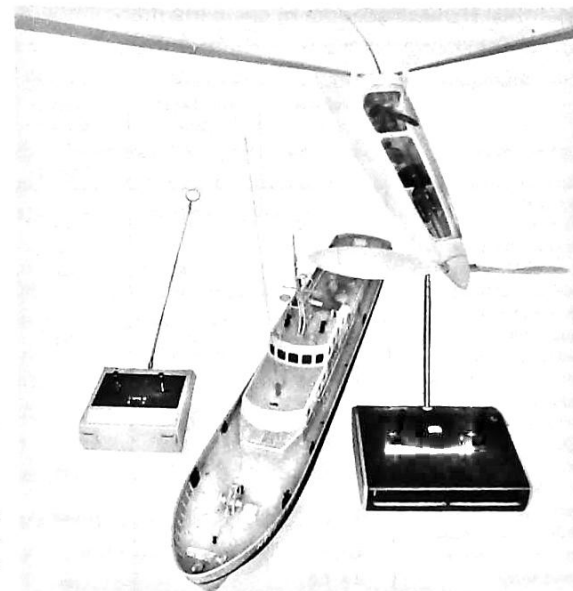| Application	Usual Voltage V	Usual Number of Cells	Mostly Inter-Mittent Use Yes/No	Capacity Of The Batteries Used Ah	VARTA Batteries Most Often Used
Motive Power and Starting	6.0 - 12.0	5 - 10	yes	1.2 - 7.00	RSH
Dictation Equipment	3.6 - 8.4	3 - 7	no	0.5 - 4.0	DKZ, RS
Powered Model Aircraft	6.0 - 9.6	5 - 8	yes	0.5 - 2.0	RSH
Video and Sound Recorders and Equipment	4.8 - 24	4 - 20	yes	1.2 - 4.0	RS, SD
Remote Control (Receiver/Transmitter)	4.8 - 12	4 - 10	no	0.15 - 1.2	DK, DKZ, RS
Photographic and Movie Film Equipment	2.4 - 12	2 - 10	no	0.2 - 1.2	DKZ, RS
Lighting for Photography	6.0 - 42	5 - 40	no	2 - 15	RS, SD
Photoflash Equipment	2.4 - 7.2	2 - 6	yes	0.225 - 4.0	DKZ, RS, SD
Portable Radio Communication Sets	6.0 - 12	5 - 10	yes	0.15 - 1.2	DK, DKZ, RS
Garden Tools (Hedge and Lawn Trimmers)	3.6 - 7.2	3 - 6	yes	1.2 - 7.0	RS, RSH
Hand-Lamps	2.4 - 6.0	2 - 5	no	2 - 7.0	RS, SD
Hobbies Generally	1.2 - 12	1 - 10	no	any	Any Series
Hearing Aids	1.2 - 2.4	1 - 2	no	0.001 - 0.5	DK, D, RS
Control Circuits for Machines and Apparatus	2.4 - 24	2 - 20	yes	any	Any Series
Medical Equipment	1.2 - 12	1 - 10	no	0.15 - 7.0	DK, DKZ, RS, SD
Measuring Instruments Of All Kinds	1.2 - 24	1 - 20	yes	any	Any Series
Model Construction	1.2 - 12	1 - 10	no	0.1 - 4.0	DK, DKZ, RS
Moped and Bicycle Lighting	2.4 - 6.0	2 - 5	yes	0.15 - 2.0	DKZ, RSX
Razors	2.4 - 4.8	2 - 4	no	0.5 - 1.2	DKZ, RS
Loud Hailers	1.2 - 6.0	1 - 5	no	0.1 - 0.5	DK, DKZ, SD, RS
Emergency Lighting and Signs	3.6 - 6.0	3 - 5	no	1 - 7.0	DKZ, RS, SD
Toys	1.2 - 6.0	1 - 5	no	0.1 - 2.0	DK, DKZ, RS
Pocket Calculators	2.4 - 6.0	2 - 5	no	0.05 - 0.5	DK, DKZ, RS
Pocket Torches	2.4 - 4.8	2 - 4	no	0.15 - 0.5	DK, DKZ
Desk-Top Calculators	4.8 - 12	4 - 10	no	0.5 - 4.0	DKZ, RS
Clock, Signal and Warning Lights	2.4 - 24	2 - 20	no	0.2 - 2.0	DK, DKZ, RS
Watches With/Without Solar Cells	1.2 - 12	1 - 10	no	0.01 - 0.05	DK, DKZ, RS
Emergency Power Supplies for EDP and Control Circuits	above 1.2	above 1	yes	See Tab. 9/5	
Powered Tools (Drilling Machines, Cutters, Shears)	4.8 - 12	4 - 10	yes	0.5 - 2.0	RS, RSH
Toothbrushes (Powered)	1.2 - 2.4	1 - 2	no	0.2 - 1.2	DKZ, RS

Table 9/4 "Applications" is a summary of the various uses of sealed cells. It shows the usual voltages and the number of cells needed (1.2V per cell). Currents consumed by the equipment are not quoted. Capacities of the cells which are suitable for each application are given in ampere-hours. The difference between regular and essentially intermittent use is an important factor to be considered. The last column lists the type letters of the suitable battery series.

There is an ever increasing demand for batteries used for uninterrupted emergency power supplies, a stationary application. The technical expertise needed for these applications is very wide ranging and, therefore, needs special treatment.

Apart from clocks and warning signs, the most important applications are:
— Electronic data processors in various forms.
— Electronic calculators and cash registers.
— Control units for automated machine tools.
— Electronic control and display units for telephones, radios and TV.
The range of applications is limited only by the capacities of the cell types available, which usually ranges from 20mAh to 15Ah.

Hence, sealed cells are preferred for low energy consuming appliances, in addition to their suitability for emergency power supplies.

All the different types can be used, but preferably the following:
— Button cells with mass plate electrodes.
— Cylindrical sintered electrode cells.
— Rectangular sintered electrode cells.
Mass plate electrode cells are suitable for low and medium loads, sintered electrode cells for heavy duty applications.

The type of circuitry and the technical design is determined by the voltage to be maintained in the event of mains failure, and the trickle charging arrangements. It should be noted that constant current trickle charging can only be used, following the voltages specified below, for an ambient temperature of 20 °C:

— Nominal voltage: 1.2V per cell
— Trickle charge voltage: 1.42V to 1.45V per cell
— Initial discharge voltage: Approx. 1.32V per cell
— End-of-discharge voltage: Approx. 0.9V per cell
— Maximum voltage for fast charge: Approx. 1.48V per cell

If it is sufficient to have a voltage stability of ± 20% relative to the nominal voltage, and when the load current is nominally constant, it is possible to use very simple charging circuits; under these conditions, the batteries can be connected directly in parallel with the load. Fig. 9/35 shows one such circuit. Because button cells can be kept on continuous charge at 0.01C A, compared with sintered cells at $0.05C_5A$, thereby needing much less current to maintain a fully charged battery, a greater part of the charger current can be used for

supplying the external load. Peak loads can be supported by current from the battery. When there is a constant external load, the trickle charger can be set to supply it, in addition to the charge current. Should the mains supply fail, the load is supplied from the battery alone. The circuitry can be considerably simplified if, for example, an electronic component must be supplied continuously at a nominal voltage of 2.4V or 3.6V and at constant current. In such cases, it is sufficient to have a standby unit consisting of a rectifier, charging resistor and the battery.

When a narrower range of voltage limits is required, voltage stabilizer circuits must be used (section 9.3). The requirements can be divided into three groups (Table 9/5).

Table 9/5:
Operational requirements for static emergency power supplies

| |
|---|
| **Light Loads:** Series DK, DKZ
Number of Cells: 1 to 10
Load: μA range over period of months to mA range for several hours. |
| **Medium Loads:** Series DKZ, RS, RSH, RSX, SD, Monoblock
Number of Cells: 3 to 24
Load: mA range over several months to A range (approx. 20A, 0.5 hour) |
| **Heavy Loads:** Series with sintered electrodes RS, RSH, RSX, SD
Number of Cells: Optional
Load: Up to 0.5 hours max. possible current approx. 90A, 3 min;
approx. 120A, 2 sec |
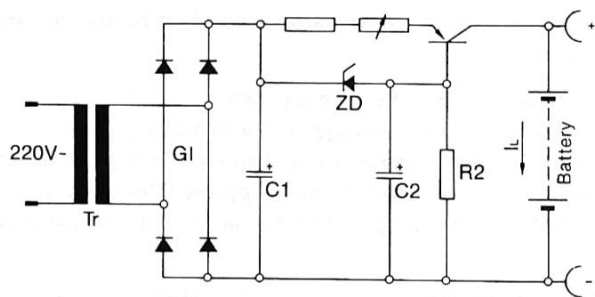
Fig. 9/35:
Charging Circuit

9.2.2 Battery Selection in Design Work
The following data is required when designing battery-powered circuits:
— Range of application (object of the design).
— Duration and level of the load.

— Nominal voltage.
— Permitted voltage limits.
— Temperature limits.
— Type of operation (cyclic or standby duty).
— Special requirements (e.g. severe environmental conditions).
— Space available.
— Battery weight.

The average load (N) in watts required for an appliance may be known, calculated or determined experimentally. The calculation involves the well known equation

$$I = \frac{N}{V} \qquad [9/1]$$

The current supply to the equipment multiplied by the required period of battery operation gives the battery capacity (C) necessary.

$$C = I \cdot t \qquad [9/2]$$

The units used in these equations are:

Load	N	in Watts	(W)
Nominal Voltage	V	in Volts	(V)
Current	I	in Ampères	(A)
Operating Period	t	in Hours	(h)
Capacity	C	in Ampère-hours	(Ah)

For values of < 1 Ah the capacity is also given in mAh (1 Ah ≙ 1,000 mAh).

After the battery series has been chosen by careful consideration of the installation requirements, the calculated capacity sets the nominal (C) capacity to be found from the capacity characteristics. This fixes the cell type; if necessary, an alternative in another series is found (e.g. 225 DKZ and 225 RS).

For applications with special temperature requirements, a larger capacity cell must be chosen; this also applies when close voltage limits have to be maintained. The number of cells required is found from:

$$\frac{\text{Nominal voltage of equipment}}{\text{Cell Voltage 1.2}} = \text{Number of Cells}$$

When the battery type has been selected, the relevant data sheets are consulted to ascertain the dimensions and weights (the data sheets are available separately).

9.2.3 Design Example

A battery is needed for a measuring instrument having the following specifications:

Nominal Voltage	6	V
Nominal Power	0.4	W
Maximum Power	6	W
(Approx. 20% of on-load period)		
Operating Period	10	h
Minimum Operating	4	V
Temperature Limits	Battery to operate down to —20 °C	
Maximum Charge Time	7	h

$$I = \frac{N}{V} = \frac{0.4}{6} = 0.07 \text{ Ampère for 10 hours} \qquad [9/3]$$

$$I = \frac{N}{V} = \frac{6}{6} = 1 \text{ Ampère for 2 hours} \qquad [9/4]$$

$$C = I \times t = (0.07 \times 10) + (1 \times 2) = 0.7 \text{ Ah} + 2 \text{ Ah} = 2.7 \text{ Ah} \qquad [9/5]$$

This example shows that a sintered electrode cell must be used because the largest mass plate cell available has a nominal capacity of 1Ah.

This load is quite low for a sintered cell so one is chosen which has a nominal capacity of about 2.7Ah at normal temperature for the required operating period of 10 hours.

Naturally, the temperature requirement complicates the matter. For the —20 °C limit, about 20% must be added to the calculated capacity so that finally approximately 3.3Ah over 2 hours is needed. By reference to the cylindrical sintered cell data sheets, a cell of about 3.5Ah nominal capacity will be found satisfactory. The nearest cell with this capacity is RSH 4, nominal capacity 4Ah.

The number of cells required is 6V divided by 1.2V, or 5 cells; there is no difficulty at the lower voltage limit because the equipment will function properly down to 4V. The choice falls on a battery of 5/RSH 4 with a plastic end cap, with strip connectors; also a charging unit supplying a current of 800mA, cutting off after 7 hours.

9.2.4 Use and Handling

Sealed cells can be used in any position. Cells which are fitted with safety valves should stand upright in a stationary application or be built in lying on their sides.

Cell maintenance is not necessary — they are maintenance-free. However, it should be noted that cells should remain clean and dry while in service, like any other electrical equipment. If cells are to be exposed to high levels of humidity, they should be protected by suitable measures, e.g. by varnishing, or by use of moisture absorbers (e.g. silica gel).

Various connectors are available for connecting the battery into the circuit, for example, welded solder tags, strip connectors, special connectors for printed circuits (section 9.1.5). Acid-free substances are to be used for flux; for soldering wire solder with 60% tin is recommended. In order to avoid unwanted heating of the cells or batteries, which could damage the plastic parts in the immediate vicinity of the soldered joint, the soldering process must be as quick as possible. Direct soldering to the case can cause damage. For soldering directly into printed circuits, only discharged cells or batteries should be flow soldered, to avoid short circuits (section 9.1.6).

Cells are in a charged state after manufacture. A long period of time can elapse before commissioning in the battery, resulting from assembly into battery stacks, storage and shipment (section 7.2.3.5). The state of charge on installation cannot be accurately defined because of time and temperature dependent self-discharge. Before use, therefore, sealed nickel cadmium batteries should be fully charged (sections 5.2 and 5.6.2).

Sealed nickel cadmium batteries can be stored for many years without trouble. Storage can be in any state of charge — fully charged, partly or completely discharged. The best storage temperatures are between 0 °C and 35 °C, with a normal relative humidity of 50%.

Cells stored for more than six months have to be charged for 24 hours at the nominal currents before installation, or at a lower current for a correspondingly longer time. After shorter storage periods, a nominal charge for about 12 hours is sufficient. If the cells have been stored in a discharged state, e.g. discharged to 1.0V per cell prior to storage, the above charging method will enable the cells to deliver full capacity.

Cells which have been stored in a charged or partly discharged state will reach their full capacity after two or three cycles of normal charge and discharge.

To obtain long useful life and trouble-free service, cells should be charged in accordance with our recommendations (section 5.6.3, 5.2 and 9.3).

9.2.5 Test Methods

Before final assembly or installation of the batteries, the user has the opportunity of removing defective cells. Some cells may have slipped through the quality control checks, and in spite of careful manufacturing and final tests do not reveal their defects until after some time has elapsed, or will not have been detected during batch sampling.

A test comprises of a visual inspection and a measurement of the off-load voltage. Whilst it is not detrimental for sealed cells to have a thin white deposit in the vicinity of the gasket, leaking cells, after quite a short period of storage, show a considerable build-up of potassium carbonate crystals over quite a large area. Such cells should not be used anymore. The off-load voltage of cells should be equal or above 1.20V, assuming the cell is not discharged completely. In case the voltage of a battery deviates by more than 5% from the average of 1.20V/cell suggests that there may be a defective cell. Such batteries should be tested before use with the following method, which is as well suitable for a random check.

9.2.5.1 Open Circuit Voltage Measurement for Comparison Checks

A significant number of cells or batteries is to be charged for 14 hours at 0.1CA and stored for 14 days at about 20 °C and normal relative humidity. The off-load voltage of a random sample, e.g. 10 cells or batteries, is measured and the mean value calculated. If one cell or battery has a voltage 5% below the average value, the cell/battery should not be used anymore.

9.2.5.2 Determining the State of Charge and Capacity Available

The charge and discharge voltage characteristic of sealed batteries is flat. Taking into consideration unavoidable variations of single cells the state of charge cannot be measured with sufficient accuracy, neither with nor without a load.

If a charged battery is needed, and there is no clear record of previous shelf time and length of use, so that the available capacity can be calculated, then an additional normal charge is recommended.

When the condition and the available capacity of a battery has to be found, the following procedure is used:

Pre-discharge at 0.2CA down to 1.0V per cell
Charge at 0.1CA for 14 hours
Discharge at 0.1CA to 1.1V per cell, or at 0.2CA to 1.0V per cell.

This capacity test gives the residual capacity available in ampere-hourse (Ah) as the product of the discharge current (A) and the discharge time t (h).

9.3 Charging Methods

9.3.1 Charging Methods for Different Purposes

The battery charging process consists of returning to the battery the amount of energy which has been previously withdrawn from it. There are many ways of fully charging a battery, some more efficient than others and some more economical than others. The user can make his choice by a decision process of elimination, carefully considering the time available for charge, whether partial or complete charge is required, the expectancy of life, what effects changing cell temperatures can be taken into account, and, last but not least, the actual cost of the charging unit.

9.3.2 Charge and Trickle Charge

Besides normal charging for cyclic operation, trickle charging may be employed, safeguarding that the full capacity is available for a long time period. The two phases of charge and trickle charge can be so arranged that one merges into the other imperceptibly but usually there is a distinct change by switching from one to the other. In such cases, the switchover from the charging phase usually takes place before a full charged state has been reached; the batteries then accept the trickle charge becoming fully charged.

9.3.3 Charging Current Characteristics

9.3.3.1 Continuous and Interrupted Charging Currents

Charging currents can flow uninterruptedly or be interrupted. They are designated as interrupted when they are stopped at any time and then may be continued, subject to certain provisos. According to this definition, continuous charging currents can show high peaks throughout their course, the criterion being that some, if only a small amount, current is always flowing. The term "pulse charge" has been adopted for interrupted charging currents during the last decade, a vogue word, which easily lets itself be associated with the concept of charging carried out by relatively short duration surges of current. In fact, the pulse rate can be a few kHz and down to 0.001 Hz or even less (for which the on/off ratio can be varied by several powers of ten). It is not only through a purely arbitrary choice of words that such very low repetition rates and charging periods of several minutes are spoken of as "pulses". Because of its large capacity (in farads), the battery has the ability to act as a capacitor in respect to pulses, acting as an integrator and storing them up so that the arithmetic mean of the pulse current, and not the pulse height, determines the charging rate, and hence the terminal voltage characteristic.

If this capacitive behaviour is not enough for integrating action, because the pulse duration is too long, then the battery behaves increasingly in the way it would under continuous charge at the same current as that of the pulse height. For this case, the term "periodic charging" instead of pulse charging will be used below.

This difference in terminology is not just a matter of words but has a practical importance; it indicates the way in which the battery absorbs the interrupted charging current. One should not, however, forget that there is a transitional region between the two types of battery behaviour defined above.

9.3.3.2 Sources of Current for Continuous Charging

Continuous charging currents are obtained from:
— D.C. power supplies (e.g. other batteries, D.C. generators, transformers with rectifiers, D.C. mains voltage dividers, etc.).
— Rectified, smoothed single or 3-phase A.C. mains supplies,

so long as the "continuity requirement" is met. That is to say that in the charging current cycle, the charging voltage V_L must always be above the battery voltage V_B if the current is to flow continuously (Fig. 9/36).
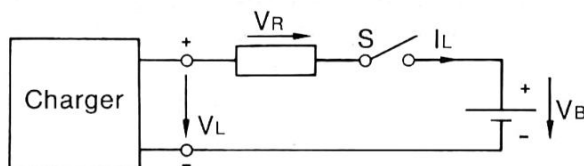

Fig. 9/36:
Fundamental charging circuit

9.3.3.3 Sources of Current for Interrupted Charging

These automatically follow when the continuity requirement is not met. The current then follows intermittently and charging pulses exist. If the internal resistance of the charger and the limiting resistor V_R in the charging circuit are low enough, the peak current can be very high. This is a deliberate aim with many charging methods, for various reasons (section 9.3.6). During periodic charging, a pre-determined break in charging is affected by switching the current on and off for a pre-determined length of time. This can be done manually, by time-switches on clocks, or by other automatic means (section 9.3.7). Besides this, in periodic charging, a minor break in the charging current can occur when during the switch-on period the voltage requirement stated in section 9.3.3.2 is not met; sometimes this is brought about deliberately.

9.3.4 Charging Rates

It is a characteristic of the nickel cadmium battery that it will accept relatively high charging rates. However, it is also desirable to keep the rate within safe limits. On the other hand, there is no objection to a high charge rate if certain precautions are taken.

Table 9/6: *Constant current charging methods for the range of sealed nickel cadmium batteries made by VARTA. The percentage accepted charge given is in terms of the nominal capacity*

Series	DK	DKZ	RS RSH	RSX	SD	Mono-block
Trickle Charge[1]						
Current	$\leq 0.01CA$	$\leq 0.01CA$	$0.03\text{-}0.05CA$	$0.03\text{-}0.05CA$	$0.03\text{-}0.05CA$	$0.02\text{-}0.03CA$
Period (h)[13]						
Charging Characteristic	Constant Current or Nominal Constant Current					
Accepted Charge (%)	100	100	100	100	100	100
Normal Charge						
Current	$0.1CA$	$0.1CA$	$0.1CA$	$0.1CA$	$0.1CA$	$0.1CA$
Period (h)	14[2]	14[2]	14[3]	14[3]	14[3]	14[2]
Charging Characteristic[4]	Constant Current or Nominal Constant Current					
Accepted Charge (%)	100	100	100	100	100	100
Accelerated Normal Charge						
Current	—	$0.15C_5A$[5]	$0.2C_5A$[6]	$0.2C_5A$[6]	$0.2C_5A$[6]	—
Period (h)	—	9.5[5]	7[6]	7[6]	7[6]	—
Charging Characteristic[4]	Constant Current or Nominal Constant Current					
Accepted Charge (%)	—	100	100	100	100	—
Fast Charge						
Current	$0.3C_{10}A$	$0.3C_{10}A$	$1C_5A$	$1C_5A$	$1C_5A$	—
Period (h)	2-2.5	2-2.5	≤ 1	≤ 1	≤ 1	—
Charging Characteristic	Constant Current or Nominal Constant Current					
	7	7	9	9	10	
Approx. Charge (%)	70	70	85-95	85-95	85-95	—
Overcharge						
Current	$0.1C_{10}A$	$0.1C_5A$	$0.2C_5A$[11]	$0.3C_5A$[12]	$0.2C_5A$	$0.1C_5A$
Period (h)	100	100	500	500	100	100
Charging Characteristic	Nominal Constant Current					

Footnotes, Table 9/6:
[1] Except for Monoblock batteries, all types can be given a fast charge (two rate charge). [2] Max. 18 h [3] Overcharge at 0.1 CA is allowed. [4] Cut-off must be time controlled. [5] $0.2C_5A$ for 7 h also possible. As a safety precaution, the charge should be terminated by a time switch. [6] $0.3C_5A$ for 4.5 h is possible. [7] Cut-off for DK cells must be at 1.49V per cell (+0.01V) and for DKZ 1.45V per cell (+0.01V). Complete charge reached with two rate charge, changeover to 0.05CA to $0.1C_5$ after reaching cut-off voltage (for temperatures between 10 °C and 35 °C). [8] Also $2C_5A$ for 0,5h with same efficiency possible. [9] Cut-off time-limited after pre-discharge or voltage-temperature limited from any state of charge. [10] Voltage-temperature controlled cut-off necessary. [11] $0.3 C_5A$ for 300h possible. [12] $1C_5A$ for 300 h also possible. [13] Without time limit.

If the current is small enough, e.g. 0.01CA, then it is possible to charge nickel cadmium batteries continuously, particularly when occasional partial discharges are carried out. Charge and trickle charge then merge into each other and the charging current can continue permanently. The process is known as **trickle charging** (DIN 40729) (32). Table 9/6, Line 1, gives the recommended trickle charging currents for the various series of sealed cells made by VARTA.

Rates of 0.1CA order of magnitude cannot be permanently accepted by sealed nickel cadmium batteries, but depending on type of cell and the period of time involved, an overcharge condition will be reached. All batteries listed in Table 9/6 can, for example, be charged at room temperature at a current of 0.1 CA for 14 hours and will have reached their fully charged state. Because this charge rate (0.1CA) at room temperature guarantees a complete charge, it is known as the nominal or standard charging current, and the corresponding name for the procedure is **normal charge** (Table 9/6, row 2).

It is now commonly acceptable to use the term "normal charge" when charging at greater than 0.1CA. The charge input and the amount that must be recharged should be in the ratio of 1.4:1. This is not really a normal charge, but an **accelerated normal charge.** It is only recommended for the DKZ series (using a charging current of $0.15C_5A$) and for cylindrical and rectangular cells (using a charging current of $0.2C_5A$) (Table 9/6, row 3). These cells are built in such a way that they can withstand the overcharge, not only up to full charge but also into the overcharge condition. Row 5 in Table 9/6 shows the **overcharge currents** permissible for the various series, and the period after which they must be switched off.

Very high rates of charge are used during **fast charging**. Here the term "fast" has to be considered relative to the cell type. Row 4 in Table 9/6 shows very clearly the difference between button cells in the series DK and DKZ (mass electrode cells), and the cylindrical and rectangular cells in the series RS and SD (sintered electrode cells).
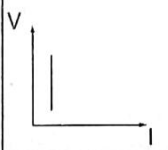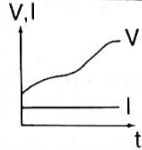
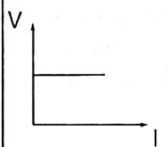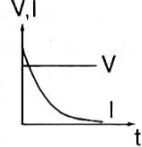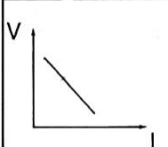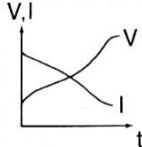### 9.3.5 The Charging Processes

9.3.5.1 Charging Characteristics
The progress of each cycle of charge is characterized by the response of the charging current to changes in battery voltage; normally the only variables in the charging circuit are the battery voltage V_B and the voltage of the charger, V_L. The charging current is determined as follows, assuming that the charging circuit is as detailed in Fig. 9/36:

$$I_L = \frac{V_L - V_B}{R}$$

[9/6]

The charging voltage V_B of a sealed nickel cadmium battery is controlled by many parameters (section 5.2 ff). The most important of these are the state of charge, the actual charging current and the cell temperature.

Table 9/7: *Charging Characteristics*

Charging Characteristics	Code	Charge/Time Graph	Application
	I		To fully charge. Safe overcharge. Manual or timed termination.
	V		Time terminated. Temperature monitored.
	W		Time terminated. Current limited to ensure a safe level of trickle charge can be achieved.

The charger voltage V_L is determined by the characteristics of the charger circuit. Hence, there are three basic possibilities with a constant resistance R in the charging circuit:

1. V_L is continuously altered in the charger in such a way that I_L remains constant, i.e. a constant current characteristic (I-characteristic).
2. V_L is kept constant at the charger, R is negligibly small. Hence the charging current is determined only by the difference between charger voltage and the battery voltage (taking into account the internal resistance of the battery). This is known as constant voltage charging (V-characteristic).
3. V_L remains constant. The charging current is, therefore, dependent on the countervoltage of the battery and the limiting resistor R. Because there is only one way of controlling the charging current, by altering the resistance of R, the method is called the resistance characteristics and the charge method is termed a nominal constant current (W-characteristic).

Table 9/7 shows these basic charging characteristics and the voltages and currents with relation to time. Only constant current and nominal constant current can be used for sealed nickel cadmium batteries, because the fundamental property of the sealed cell is that after full charge has been reached, the terminal voltage actually starts to fall. Stable conditions can, therefore, not be reached when a constant voltage technique is used with these batteries.

The charging at constant current, **I-characteristic**, is the most important of the three methods for sealed nickel cadmium batteries because it results in the best defined charging characteristics and is the only method that can be used when the capacity is being checked, and comparative measurements made.

A nominal constant current, **W-characteristic**, can be achieved at significantly less cost on complicated chargers than the constant current charge because the charging current is continuously self-regulating. By a suitable choice of the limiting resistor R, the initial charging current can be set to a suitable value, and later the trickle charge will not exceed the value stated in Table 9/6, row 1. It should always be considered as a cost-advantageous substitute for the constant current charge.

The constant current charge (and the corresponding nominal constant current charge) can be used in its basic form only for trickle charging. In all other cases, some modifications of the basic characteristic are needed.
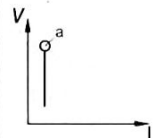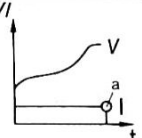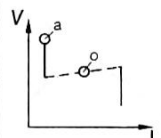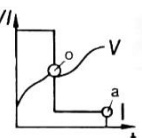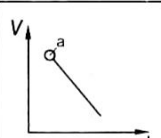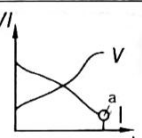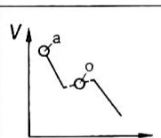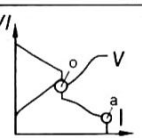
9.3.5.2 Modified Basic Charging Characteristics
Trickle charging is only recommended at charge rates that can be allowed to flow for an unlimited period. At normal charging rates, at accelerated rates, and at fast charge, the end of the charging process must occur at a definite point in time. The charging characteristics and the rate of charge with respect to time are given in rows 1 and 3 in Table 9/8. The modified point of charge is a point "a" (I_a, W_a).

Cut-off can be manual, controlled by a time switch, or in response to a signal from a sensor (e.g. voltage, temperature). With **cut-off in response to a voltage signal**, it is essential that this cut-off voltage will definitely be reached before the battery is fully charged. Because the charging voltage characteristic of nickel cadmium batteries reduces as its temperature increases, it is necessary as a rule to have an automatic temperature compensation to adjust the cut-off voltage of the charger determined by the battery temperature. The cut-off voltage related to the temperature is normally arranged so that there is a linear relationship between cut-off voltage and temperature, as Fig. 9/37 shows. It is usual to quote the cut-off temperature for 20 °C and the slope of the characteristic in millivolts per °C. This slope is also known as the temperature coefficient of the cut-off characteristic. The temperature coefficient is dependent on the battery type (section

5.2.6), on the charging current used, and must, therefore, be specially set for each charging method. The actual battery temperature can be sensed by the electronic control circuit in the charger, which is fed with signals from a temperature-sensitive resistor attached to the warmest part of the battery. A cell connector can often be used for this purpose.

Table 9/8:
Modified charging characteristics

Charging Characteristic	Code	Charge/Time Graph	Application
	I_a		— For large sealed cells where cells would overheat during overcharge. — For quick charge. — For fast charge.
	$I0I_a$		— For partial charging to a predetermined voltage at a high charge rate followed by fully charging at a lower charge rate.
	W_a		— For low cost unsophisticated charging systems.
	$W0W_a$		— For low cost unsophisticated charging systems.

The tripping voltage is, in practice, so chosen that for each temperature, the charging current is approximately half way between the sharp voltage rise occurring towards the end of charge and the voltage maximum reached after continued charging (Fig. 9/38).

The disadvantage of voltage-controlled cut-off is that at the point the charge is terminated, the battery is not fully charged (Table 9/6). However, this could, on the other hand, be an advantage in that no excessive temperature and pressure occurs, and that the method always gives a satisfactory Ah-efficiency as a result of the reduced charge factor involved.

The battery may be fully charged by allowing a residual charge to continue, if necessary at the trickle charge rate (section 9.3.5.3).

Fig. 9/37:
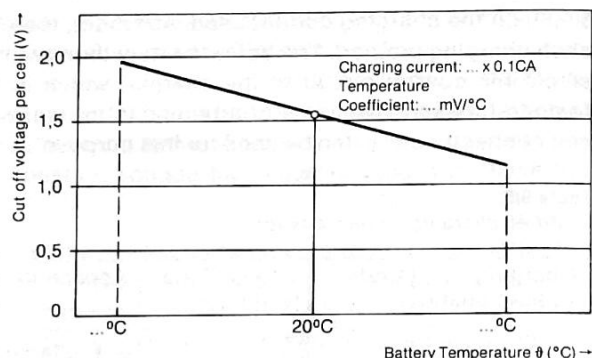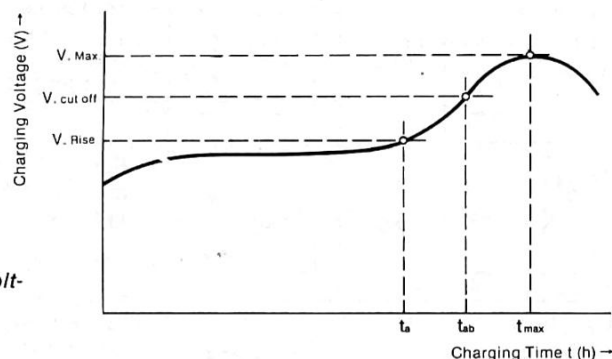*Example of a cut-off characteristic of a voltage-controlled constant current charge*

Fig. 9/38:
Locating the cut-off voltage point

9.3.5.3 Combinations of Basic Charging Characteristics

Two typical combinations are shown in items 2 and 4 in Table 9/8 (I0Ia, W0Wa). As soon as a pre-determined charging voltage has been reached, the battery is changed to a lower charge current by increasing the value of the limiting resistor. The change-point is indicated in the diagrams by the small circle.

### 9.3.5.4 Charging with Temperature Dependent Characteristic: The TGI-Charge

The TGI-charge is partly based on constant current characteristics, but the actual charging current is changed by battery temperature signals — i.e. it is a Temperature-Governed-I-Charge. This charging process was developed by VARTA engineers specially for applications which involve severe variations in battery temperature.

The dependence of charging voltage on temperature has been noted in the sections above. With a strictly regulated charging current this can lead to the following:

— at low temperatures the major charging phase is terminated prematurely, because the permitted upper limit of the cell voltage ($\leq$ 1.6 V per cell) is reached.

— at high temperatures the cell is not fully charged for the same reason because the charging current cannot cause a cell voltage rise near the end of the charge.

These disadvantages can be overcome by arranging for the charging current at the temperature concerned to be so adjusted that an approximation of the ideal voltage characteristic for sealed batteries will be consistently attained, as shown in Fig. 9/39. If this adjustment is made automatically then the battery can safely be charged using the TGI-charge method.

Fig. 9/39:
Ideal charging characteristic for sealed nickel cadmium batteries
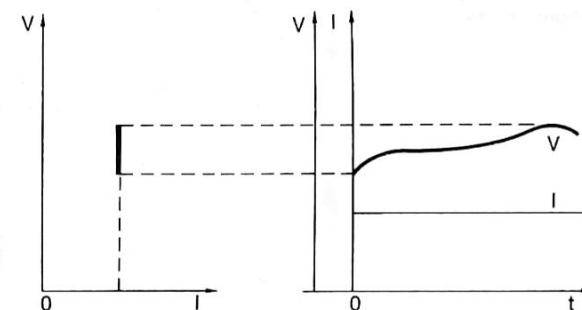
The reason why this charging method not only effectively suppresses undesirable side effects and, therefore, leads to high Ah-efficiency, particularly at higher temperatures, will be discussed below in more detail.

Fig. 9/40 shows the typical charging sequence for the constant current charge at different rates for temperatures of —10 °C, 20 °C and 40 °C using a rectangular nickel cadmium battery SD 15 (nominal capacity 15 Ah). Consider the sequence for the charging rate $0.1C_5A$ or 1.5 A, using the normal charge factor of 1.4 (Table 9/7).

At 20 °C, this current gives a charge which has a distinct voltage rise towards the end of the charge, when about 130% of the nominal capacity has been accepted, leading to a smooth transition into the overcharge region where the current causes oxygen to be evolved. A 1.4 charge factor is therefore reasonable.

At 40 °C, the relationships are less satisfactory; the gassing phase has started when 75% of the nominal capacity has been accepted, reducing the charging voltage. At this point, therefore, overcharge has, in fact, started and if charging is continued to the charge factor of 1.4, no useful work is performed and there may even be damage to the battery. A greater amount of capacity has been inserted than the battery can return, as electrical energy has been converted into heat.

At -10 °C, on the other hand, when charging at $0.1C_5A$, after about 100% of the nominal capacity has been inserted, the critical cell voltage of 1.6 V for hydrogen evolution has been reached. A charge factor of 1.4 would, in this case, certainly lead to damage.

Fig. 9/40:
Charging voltage characteristic with respect to capacity input as % of nominal capacity (C) in Ah for cell type SD 15 K at different charging rates and temperatures
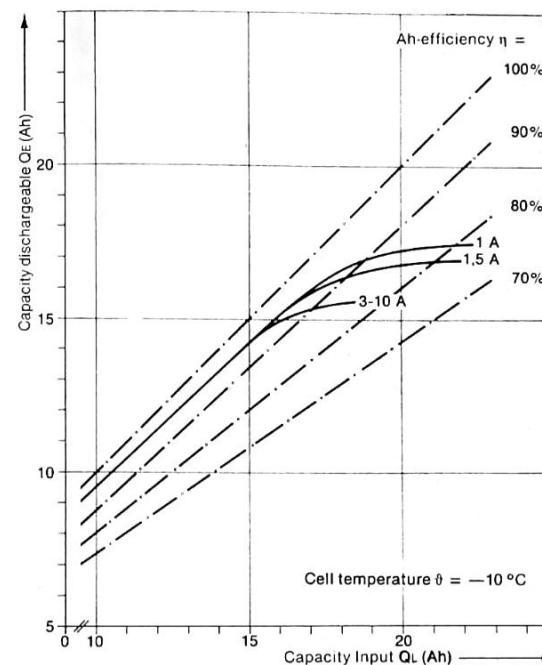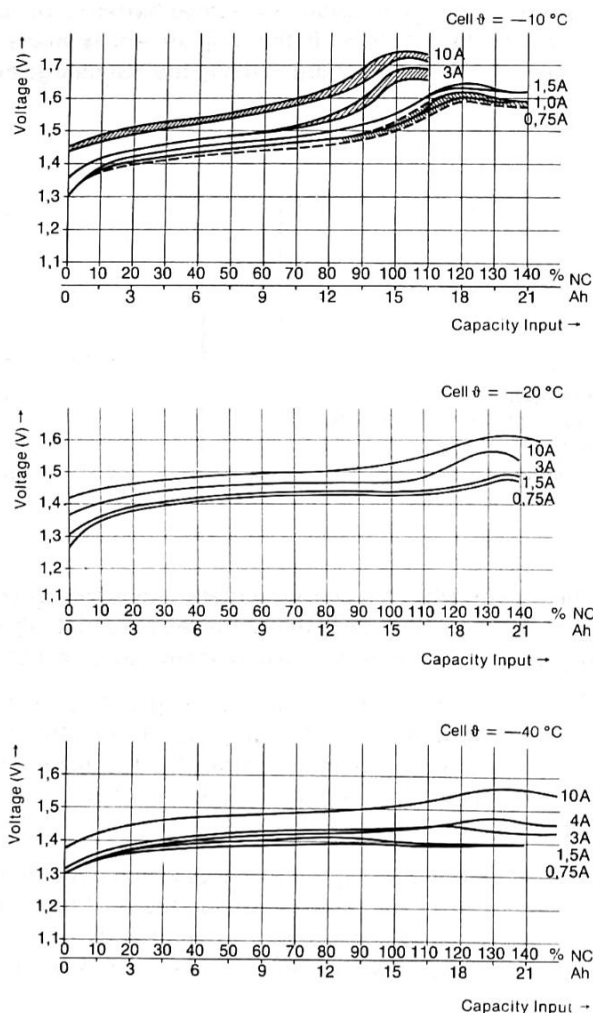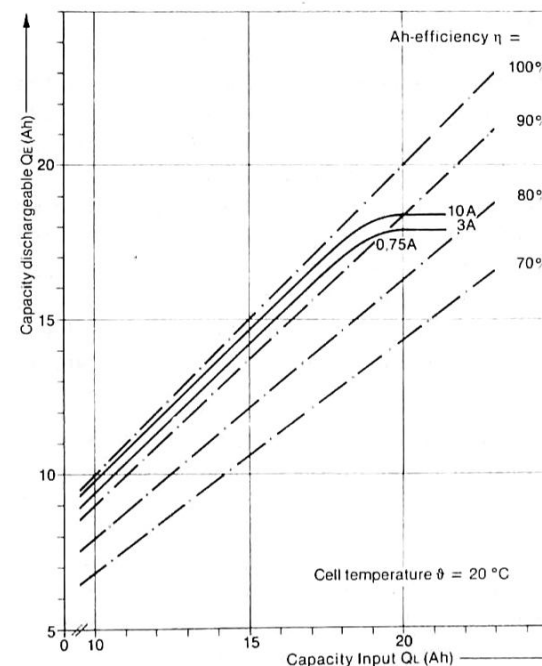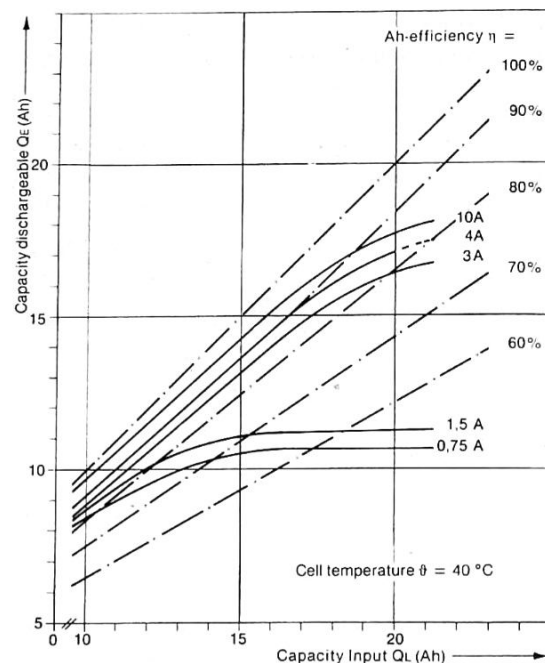

Fig. 9/41:
Capacity dischargeable as a function of capacity input for various charging rates for a SD 15 K cell at different temperatures (discharge at 6 A = $0.4C_5A$ to 1.0 V after standing for 1 h)

Ah-efficiency η =

100%
90%
80%
10A
4A
3A
70%
60%
1,5 A
0,75 A

Capacity dischargeable Q_E (Ah)

Cell temperature ϑ = 40 °C

Capacity Input Q_L (Ah)

Inspection of Fig. 9/41 leads to the same conclusion. The graphs show the connection between capacity input Q_L and the corresponding dischargeable energy Q_E for charging periods of different durations at −10 °C, 20 °C and 40 °C. Superimposed is a series of broken lines showing Ah-efficiency which enables the Ah-efficiency of the charge/discharge cycles concerned to be read off without the need to calculate. For an Ah-efficiency of 100%, the curve plotted must coincide with the Ah-efficiency line for 100%. The point where the plotted curves turn towards the horizontal indicates the point where overcharging starts to take over from the charging phase. Overcharging does not occur until the horizontal sector is reached; continued charging beyond this point reduces the Ah-efficiency.

Fig. 9/41 shows that with a $0.1C_5A$ rate at 20 °C the battery will charge up to 120% of the nominal capacity with an excellent Ah-efficiency and thus a utilization of the capacity cannot be improved. In contrast to this, the $0.1C_5A$ rate of charge at 40 °C is quite unsatisfactory. At this current and temperature, the cell accepted only about 75% of the nominal capacity, and after that is in the state of overcharge, giving very poor Ah-efficiency. At −10 °C, however, $0.1C_5A$ is too high: beyond a capacity input of about 107% of nominal capacity, the Ah-efficiency likewise decreases rapidly; in this instance, it is

not oxygen evolution that causes the lower efficiency, but hydrogen. Turning back to Fig. 9/38, it can be seen that at this point in the charging phase, the permissible limit of 1.6 V charging voltage has been exceeded.

If one now considers the other charging currents shown in Figs. 9/40 and 9/41, it is possible to find that much better relationships are obtained with rates below $0.1C_5A$ at lower temperatures, and above $0.1C_5A$ at higher temperatures.

Fig. 9/42 has been constructed from the results given in these figures, to show the TGI characteristic for the SD 15 K battery. If the charger is regulated so that it automatically gives constant current with changing temperature, following the TGI characteristic, then the following will apply:
— The charging rate adjusts itself automatically so that for any cell temperature the unwanted side effects are kept to a minimum; this leads to an optimum Ah-efficiency charging.
— The charging rate is always regulated in such a way that towards the end of the charge it causes a marked step in the cell voltage to appear which can provide a clear signal that full charge has been reached. Hence, the cut-off voltage characteristic can be relatively flat, so that at high temperatures the voltage-controlled cut-off operates just before full charge is reached. When the main charging phase is terminated at this point and there is no overcharge, the Ah-efficiency will not decline and there will be no harmful cell heating.
— The cell capacity is utilized at almost optimum efficiency over the whole temperature range covered by the TGI characteristic.
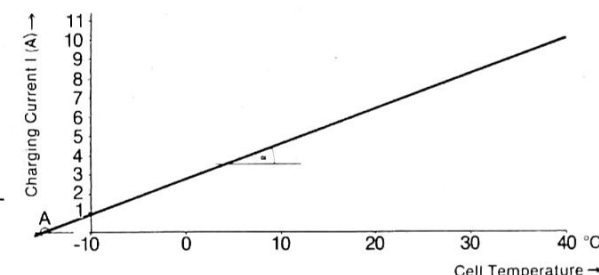
Fig. 9/42:
TGI characteristic for SD 15 K battery
A = TGI zero point
α = Slope of TGI characteristic

The TGI-charge is particularly recommended for batteries that must operate in conditions where severe temperature changes occur and when large sealed cells above 15 Ah capacity are used.

For continued charging after the cut-off voltage has been reached, it is best to use the interrupted charge method described in section 9.3.7.3 and 9.3.7.4, when the TGI current is also used as the interrupted charging current.

9.3.6 Pulse Charging

9.3.6.1 Purpose and Definitions

With pulse charging no continuous current is applied to the battery, but pulses of current at frequencies from about 1 Hz up to about 3 kHz. The pulse duty factor (ratio between pulse duration and period cycle) can vary between 1:1 and 1:5. Pulses can have very varied waveform, but the peak values are mostly multiples of the normally used continuous charging current.

There are several reasons for using pulse charging; some of the most important are:

— Reduction of charging time with good (approaching 100%) battery capacity and without harmful heating of the cells.
— To achieve a reconditioning effect at partly passivated electrodes.
— To obtain the same charging voltage characteristic and the same utilization of capacity as with TGI charging, by using a pulse train of similar peak values. Thus, for example, the TGI charging effect would be obtained with a current of smaller mean value.

There would be good reason for adopting the pulse charging method if only one of these objectives were realized. From various viewpoints, i.e. those of charging unit manufacturers, and of the users, many statements about the results that can be achieved have been made. It is, therefore, appropriate to conclude with an account of the different pulse types used and the operating experience gained in an independent laboratory test programme, as well as VARTA's experience with these charging methods. The reader can then easily decide for himself whether it would be to his advantage to use pulse charging methods.

9.3.6.2 Pulse Types
Rectangular Pulse

American practice is to use the narrow rectangular pulse types shown in Fig. 9/43. Whilst the direction of the positive-going pulse is easy to obtain with simple charge circuitry, the negative-going additional pulses in the other two types involves an amount of extra expense; in the opinion of the charger manufacturer, the negative pulse should reduce the formation of polarizing surface layers which could impede the passage of the current.
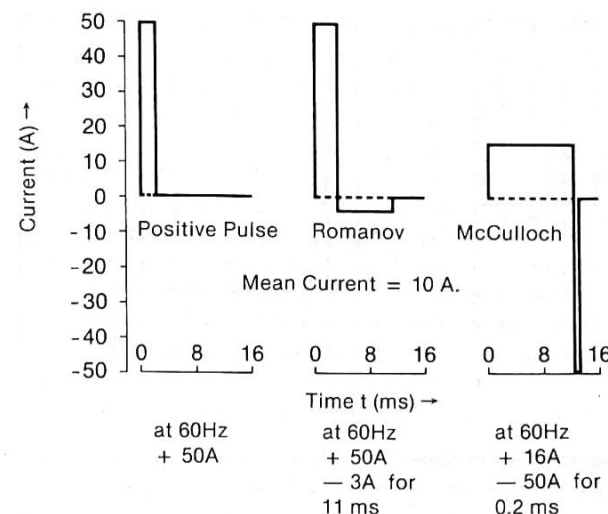
Fig. 9/43: *Various Rectangular Pulses*

	at 60Hz	at 60Hz	at 60Hz
	+ 50A	+ 50A	+ 16A
		— 3A for	— 50A for
		11 ms	0.2 ms

Half-Sine Pulse

This can be very simply obtained by charging the battery with rectified single- or three-phase A.C. mains. A single phase method is used for the VARTA TSL charging process (Section 9.4.4.3). A typical pulse train is shown in Fig. 9/44, and is produced by full-wave rectification.
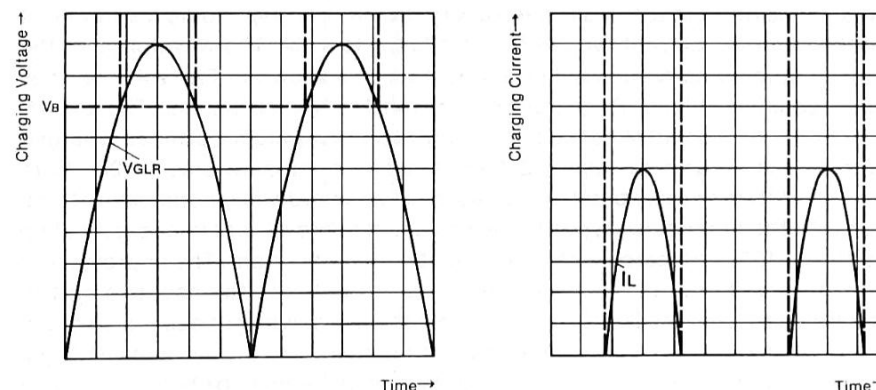
Fig. 9/44:
Half-sine pulse charge (Full-wave rectified A.C.)

Other Pulse Types

Triangular pulses can be obtained from D.C. supplies by using integrating circuits. Fig. 9/45 shows one example of this type of pulse. Further variations can be obtained when the pulse train is generated by rectification of 3-phase mains together with phase-controlled switching.

Fig. 9/45:
Triangular pulse for charging from D.C. supply

9.3.6.3 Operational Experience with Pulse Charging

A United States Army testing establishment (USA ECOM) (33) has recently investigated the charge acceptance at the positive and negative electrodes of open nickel-cadmium batteries and equivalent completely sealed batteries and has compared the behaviour of the two types when charged with a constant current. The pulse frequency used ranged from 30 Hz to 3 kHz, and the duty cycle was varied by varying the pulse width. The height of the pulses was varied 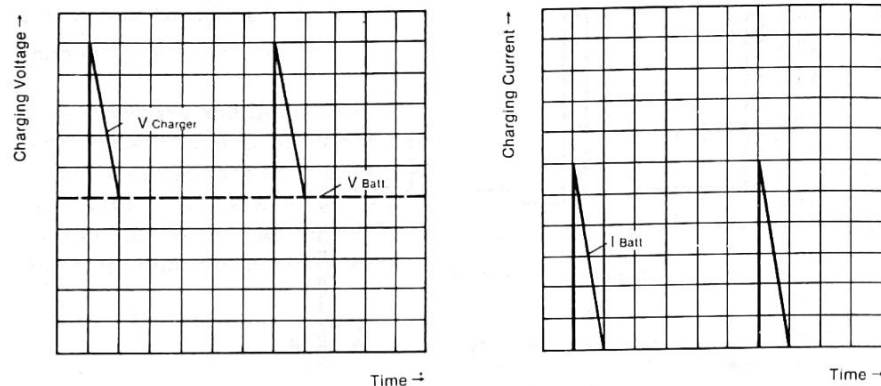during the tests in such a way that the corresponding mean values of the charging current ranged from 0.125 CA to 4 CA. The waveforms of the pulses studied corresponded (at 60 Hz) to those shown in Fig. 9/43, i.e. they were positive pulses, Romanov pulses and McCulloch pulses. The experiments yielded positive results for open nickel cadmium batteries charged with average currents (about 2 CA) at average temperatures (—20 °C to 30 °C). With the purely positive pulses there was hardly any noticeable effect, but with the other pulse types there was a real improvement in capacity of up to 10%—15% compared with charging at constant current. The improvement was observed in both electrodes and was attributed to the negative part of the Romanov and McCulloch pulse types; the effect was not caused so much by the actual shape of the negative pulse but merely to the amount of "negative energy" involved, for which the optimum was found to be between 2 mWs and 2.5 mWs per pulse.

Charging experiments with positive-going pulses on the other hand gave a quite different and unexpected effect, which was specially noticeable in the negative electrode of "aged" cells. During the charging cycle the coarse crystalline structure responsible for the loss of capacity of the active mass was reduced to a fine-grained state again and the capacity nearly regained its nominal value.

Detrimental effects on the cells after prolonged pulse charging/discharge cycles could not be established, but neither was the avoidance of the second step in the discharge characteristic, nor the well known memory effect, as had been hoped. The only improvement here was the usual "reconditioning" brought about by deep discharge. A repetition of the tests using sealed nickel cadmium cells did not yield the same result. For these tests, pulse charge currents of mean values 0.125 CA, 0.5 CA and 2 CA over the temperature range of —40 °C and 50 °C were used.

The extractable capacities were the same as for charging with the equivalent direct currents. The charging voltage characteristic, internal cell pressure and the cell temperature were all similar. These results are grounds for concluding that with sealed nickel cadmium cells a reduced strength diffusion barrier builds up when as compared with open cells.

The extensive series of tests on sealed nickel cadmium batteries of the SD 15 type carried out by VARTA engineers were performed with positive pulses as shown in Fig. 9/46. These were intended to show whether, with rectangular pulses of peak value corresponding to the TGI current detailed in Fig. 9/42, the same effect on the charging voltage characteristic, Ah-efficiency, and extractable capacity can be obtained as can with the TGI charge. The experi-

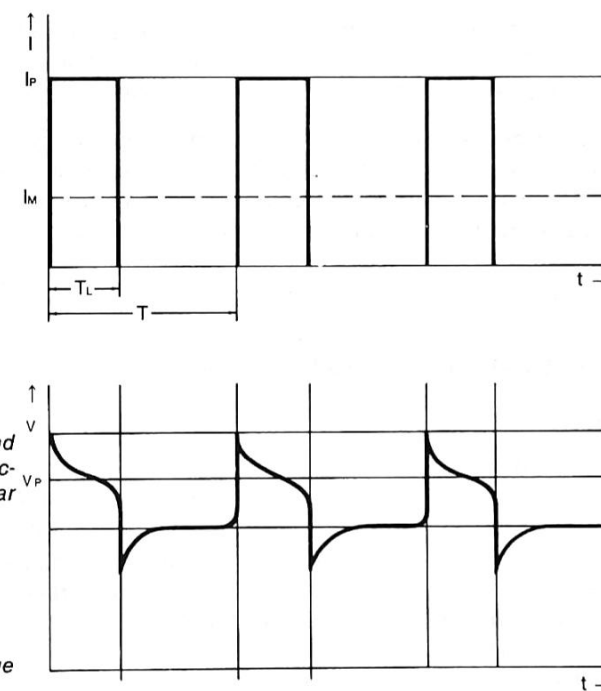**Fig. 9/46:**
Charging current and charging voltage characteristics for rectangular pulse charging,
$f = 1/T$
Duty cycle $= T_L/T = 1/3$
$I_P =$ *peak pulse current*
$I_M =$ *arithmetic mean of the pulse current*
$V_P =$ *pulse charge voltage*

ments were performed at temperatures from −10 °C to 40 °C; at −10 °C the peak value of the pulse was 0.05 C_5A, corresponding to the TGI characteristic, and at 40 °C, 0.6 C_5A. The pulse frequency ranged from 0.001 Hz to 2 kHz, the duty cycle from 1:1 to 1:4.

The series of experiments led to the following conclusions:
— During charging, the cell voltage over the temperature range −10 °C to 40 °C during pulse is always lower than during constant current charging. Over the middle frequency range from 1 Hz — 100 Hz, the pulse charge voltage behaved as if a constant current of the arithmetic mean of the pulse charge current were used. This signifies that the more the pulse charge voltage for the same peak pulse level changes from the TGI charge current, the greater is the charge ratio.
If the frequency is increased at constant charge ratio, then the pulse charging voltage is slightly increased, however, from here onwards it remains below the TGI charge voltage. Below 1 Hz, there is no further rise in the pulse charging voltage. If the pulse rate is reduced below 1 Hz, then for constant charge ratio a rise in the pulse charge voltage is seen, particularly when approaching the region in which the pulse, due to its length, acts as if it were a constant current of limited duration. This applies to the case when the current pulse flows, at least, for minutes.

— The Ah-efficiency and the capacity obtained for the temperature range −10 °C to 40 °C are the same as for a charge at a constant current of value equal to the arithmetic mean of the pulse charge current.

Hence pulse charging offers no improvement, but also no worsening of charging behaviour compared with charging at the equivalent direct current. If the TGI effect is to be obtained then the arithmetic mean of the current pulses must be equivalent to the TGI currents as shown in Fig. 9/42.

9.3.7 Trickle Charging Methods

9.3.7.1 Introduction
A trickle charge is a continuous charge used to maintain batteries in a fully charged state. Its purpose is, therefore, to compensate for losses caused by self-discharge. Self-discharge is a continuous temperature-dependent chemical reaction on the electrodes of off-load batteries, which without a trickle charge would eventually lead to a total discharged battery; this naturally cannot be tolerated if the battery is to be always available for use, as for example in the case of standby power supplies.

Difficulties in determining a suitable method for the trickle charge are caused by the temperature dependence of the self-discharge. The simplest answer would be to connect the battery to a trickle charger having a constant voltage equal to the open-circuit of the battery. This procedure, however, cannot be applied to sealed nickel cadmium batteries due to the fact that the charging voltage actually decreases with an increase in temperature. Therefore, the solution is to charge sealed nickel cadmium batteries at a rate which they will accept without being damaged.

In practice, there are several different methods of trickle charging, the most important of which will now be described.

9.3.7.2 Trickle Charging with Low Currents
With this method, a nominal constant current is supplied to the battery for long periods. Table 9/6 gives brief information on this method and the current recommended for the different types of VARTA batteries.

Trickle charging at low rates is the most widely used method for these purposes because only a very simple charger is needed. By using a current chosen from the rates given in Table 9/6, it is possible to ensure that no unacceptably high cell voltage will occur down to a temperature of approximately 0 °C.

Fig. 9/47:
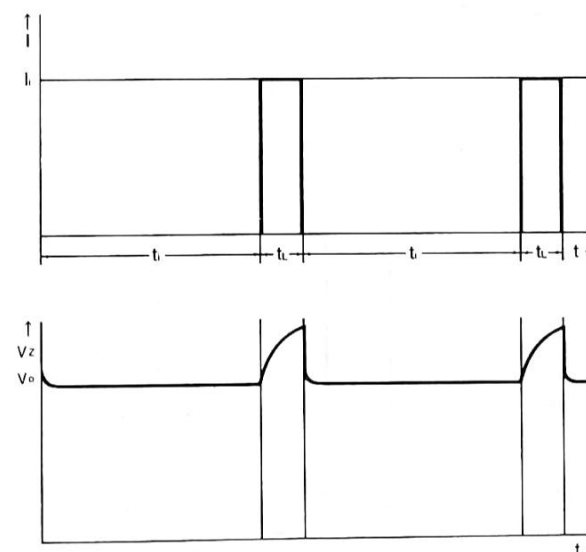Intermittent charging, charging rate (above) and charging voltage characteristic (below)

A disadvantage of charging at a fixed rate is that it is only possible to match the charging to the temperature-dependent self-discharge over a limited temperature range. At low temperatures, it leads to increased evolution of gas, and at higher temperatures, e.g. above 30 °C, it is not able to compensate for

that part of the self-discharge to which the decomposition of higher valence nickel oxide is attributed, because it cannot raise the cell voltage to the necessary level (section 9.3.4). Therefore, a lower temperature limit has to be applied when trickle charging at low rates and also remember that only a part of the cell capacity can be extracted at higher temperatures.

Another undesirable effect can be noticed when sealed batteries are trickle charged at low currents. This is the second step in the discharge characteristic, which has already been described in detail in section 5.6.1.3.

9.3.7.3 Intermittent Charging
With this method, trickle charging is applied for limited periods at pre-set times. The longer the interval between charge, the greater can the charging current be. There are certain limits for the intervals between charges and the rate of charge. It is satisfactory to have a 2 minute charge per hour (Fig. 9/47). Because the rate of self-discharge is temperature-dependent, the same applies for the intermittent charging current. This will, therefore, be chosen on a basis of the TGI characteristic shown in Fig. 9/42. If intermittent charging is supplied from a TGI charger (section 9.3.4), then the intermittent charging of sealed batteries can be performed under optimum conditions over a wide temperature range. By intermittent charging, full charge can also be reached, as described in section 9.3.3.1.
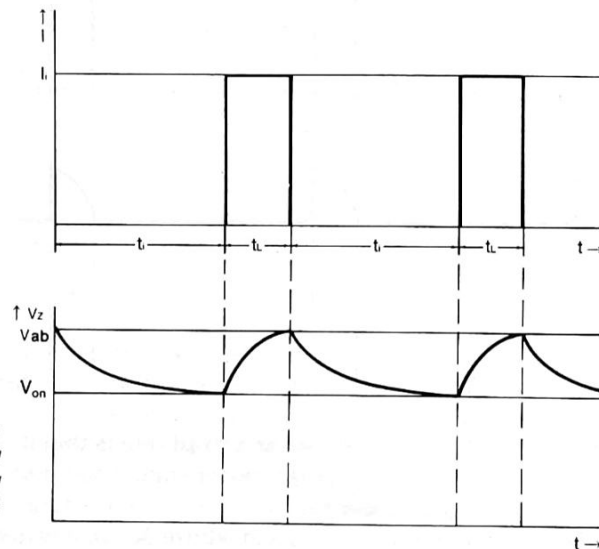
Fig. 9/48:
Charging between two voltage levels; charging rate (above), and charging voltage characteristic (below)

9.3.7.4 Charging Between Two Voltage Levels

With this method, charging is carried out as shown in Fig. 9/48. During charge, the cell voltage rises to the upper level, at which point the charging current is cut off until the cell voltage has fallen to the lower limit, when it is switched on again, and so on. It may be necessary to arrange for the cell to reach the lower voltage limit more quickly by switching the cell to an external load for brief periods. This procedure can be used satisfactorily with open nickel cadmium batteries but should not be used with sealed types because on thermal principles the behaviour is likely to be uncontrollable.

9.3.8 Parallel Charging
When a battery consists of several units it is the question whether the units can be connected in parallel during charge and discharge. Whilst direct parallel connection is satisfactory for the discharge phase, this is not satisfactory.

Fig. 9/49:
Charging in parallel with separate chargers

Fig. 9/50:
Charging in parallel with a single charger

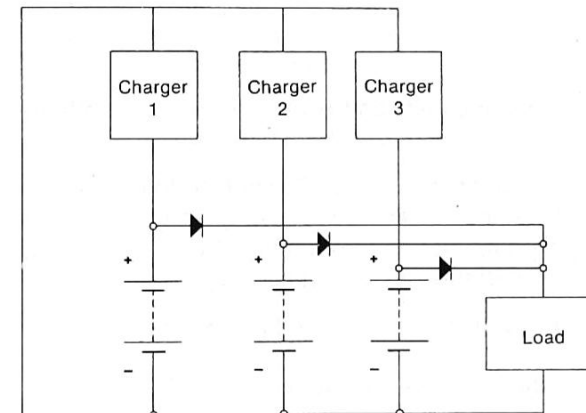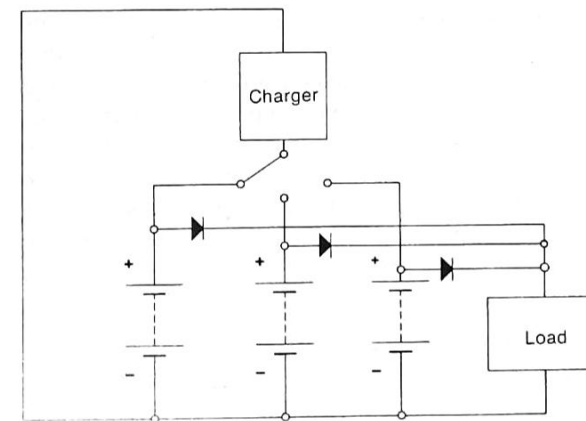factory for charging and there is no choice but to have a separate charger for each battery unit. For the condition that the load is to remain connected to the batteries the units must be electrically separated by diodes as shown in Fig. 9/49. Charging of each unit is then by the selected method, each battery having its own charger. As an alternative, each battery can be charged on a rotating basis from a common charger as shown in Fig. 9/50. For discharge in parallel, the state of charge of individual units is not critical; at any time the battery with the highest state of charge supplies the bulk of the load current until its terminal voltage falls to that of the others in the bank.

9.4 Charging Units and Charging Circuits

9.4.1 Introduction
VARTA can supply complete charging units and advice on charging methods for all commercially available sealed nickel cadmium batteries.

The chargers are designated by short titles, e.g. charge box, followed by a type number consisting of letters and numerals. Table 9/9 gives the key to the letters used for all VARTA charging and rectifier units; letters of particular significance to nickel cadmium batteries are underlined.

The letters are placed in alphabetical order in the type number, the only exceptions being
— Z with a hyphen in front of the complete type number
— D and E in front of the load specification.

All capital letters are placed in front of the numerals for the load specification, which consists of numerals in front of the oblique stroke for the voltage rating in volts (in multiples of 1.2 V per cell for sealed nickel cadmium batteries), and numerals after the oblique stroke to signify the charging current in amperes, which is related to the nominal voltage of the charger, and determined in multiples of approximately 1.4 V per cell under charge. All lower case letters are arranged according to the load specification. Thus the letter "x" always appears in the last position to indicate suitability for sealed nickel cadmium batteries.

Chargers currently available from VARTA and specially suitable for sealed nickel cadmium batteries are described below, together with their operation. This information is naturally subject to regular changes as a result of continuing design development.

Table 9/9: *Letter Code for VARTA Charging and Rectifier Units*

A Emergency exit signs

B Rectifier unit with internal or external batteries

C

D Rectifier unit for three phase mains

E Rectifier unit for single phase mains

F Charger for battery-powered vehicles

G Charger for sealed cells

H Rectifier unit with blocking cells

I Charger for commissioning of cells

K Rectifier unit for operating theatre lighting supply

L Trickle charger or rectifier unit with trickle charging section or facility

M

N Mains rectifier unit

O Emergency lighting switchover device

P Charger for fast charge

Q Charger for trickle charging (buffer batteries)

R Hot cathode gas-filled low voltage rectifier

S "Advanced technology" charger

T Charging board

U Cell switch

V Charger with circuit based on ALV leaflet 301 units

W Water deionizing unit

X

Y Security beam unit (only for units made to ALV leaflet 105)

Z Special model (always used for specially designed unlisted units, placed in front of the type number

a Corresponds to "o"

b

c Self-regulating rectifier with cut-off choke

d Rectifier unit with toroidal choke

e Rectifier with continuously adjustable output characteristic

f Air-cooled rectifier unit with blower

g Rectifier unit with smoothing circuit

h Charger with manual selection of alternative output, e. g. fast charge or trickle charge

i Charger with no isolation between mains and battery (e. g. charger in capacitor circuits)

k Constant current charger

l

m Magnetically controlled rectifier unit

n Rectifier unit with mains phase monitoring device

o Rectifier unit with automatic relay-operated changing of charging characteristic

p Charger with protection switch

q Charger with high leakage transformer

r Regulated charging unit (e. g. constant voltage: ± 1% accuracy)

s Phase-controlled rectifier unit

t Semiconductor-controlled rectifier unit

u Rectifier unit with output adjustable in steps

v Rectifier unit with simple regulator (e. g. constant voltage ± 1% accurracy)

w Charger with time control switch

x Charger for nickel cadmium batteries

y Charger for nickel iron batteries

z Charger for periodic changeover charging of two batteries

9.4.2 Trickle Chargers

All universal chargers (uni-chargers) and multi-charger types as described in Table 9/11 together with their technical specifications can be used for this purpose although this is not specifically stated. They can be pre-set to give the recommended trickle charge for stationary installations. In Uni-chargers there is a coarse adjustment of the charging current selected by the range switch, together with fine adjustment obtained by variable resistor control in conjunction with a calibrated ammeter connected in series with the batteries on charge. With the Multi-charger types the required trickle current can be selected directly from the different sockets fitted on the panel.

The universal chargers Uni I to III allow the connection of 1 to 10 cells, Uni IV, 1 to 20 cells. Because all units are protected against short circuit, the number of cells connected is not important.

Further particulars of these units are given in section 9.4.3.3.

9.4.3 Chargers for Normal and Accelerated Normal Charging

9.4.3.1 Introduction

As mentioned in section 9.3.4, normal charge is perfectly satisfactory because it always results in full charge when the charge factor of 1.4 is used. With this method the charging phase continues beyond the full charge point into the overcharge region. Control is maintained over the charge supplied when the charge is based on the constant current characteristic, either for 14 hours at 0.1 CA, or by using the accelerated normal charge 0.2 CA for 7 hours (Table 9/6).

Normal charging can also be achieved using a nominal constant current (W-characteristic). Because this method involves a charging current with a falling characteristic, the initial charging current is set at 0.12 CA or 0.24 CA. The charging current then falls below the nominal charging rate as the battery voltage rises.

Therefore, in the following sections both nominal (I-characteristic) and full constant current (W-characteristic) chargers are considered.

9.4.3.2 Socket Chargers — To Take Cells and Batteries

As Figs. 9/51 and 9/52 show, these are chargers combined with plugs which can be plugged into sockets for charging at suitable currents. They have been designed to have very little overall weight. This has been achieved by using transformerless circuits as shown in Figs. 9/53 and 9/54.

Because these chargers are not electrically isolated from the mains, they are constructed to the mandatory safety precautions specified in VDE "Protection Insulation, Protection Class II" so that all parts carrying electricity are fully insulated. The housing for the batteries on charge is designed so that the batteries cannot be inserted in reverse polarity.

Table 9/10 gives a summary of currently available socket chargers made by VARTA.

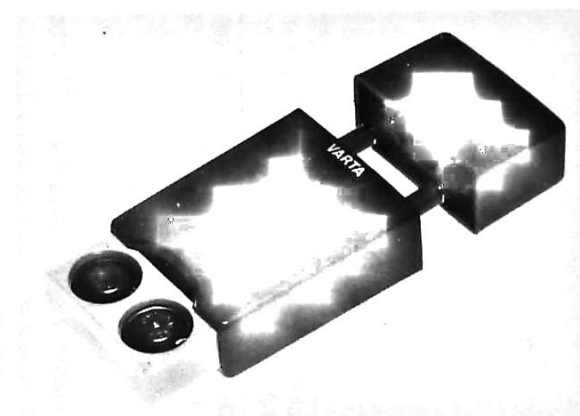**Fig. 9/51:**
Socket charger for 1 to 2 button cells, type 20 DK. A similar design is used in the charger for 1 to 2 type 10 DK button cells
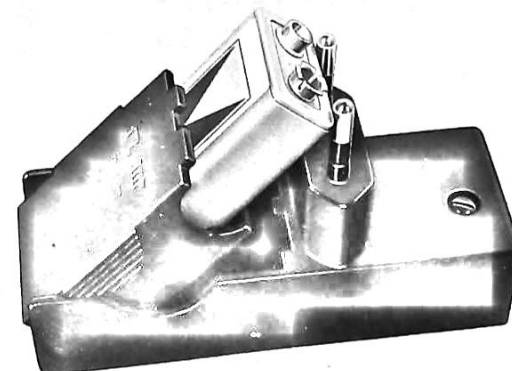

Fig. 9/52:
Socket charger for battery type TR 7/8. A similar design is used for battery 4/100 DKO

Table 9/10:
Socket Chargers

Type		Socket Charger 1-2 x 10 DK	Socket Charger 1-2 x 20 DK	Socket Charger 1-2 x 50 DK	Socket Charger Tr 7/8	Socket Charger 4/90 DKO	Socket Charger 2 x 151 D
Type Number		GE 2 x 1.2/ 0.001 ix	GE 2 x 1.2/ 0.002 ix	GE 2 x 1.2/ 0.005	GE 8.4/ 0.009 ix	GE 4.8/ 0.009 ix	GE 2 x 1.2/ 0.015 ix
Charging Current	(mA) 50 Hz	1	2	5	9	9	15
A.C. Mains Voltage		110/220 V	110/220 V	110/220 V	110/220 V	110/220 V	110/220 V
Dimensions Length x Width x Height	(mm)	60x33x17	60x33x17	82x53x60	100x36x62	82x53x60	82x53x60
Weight	(g)	20	20	65	50	60	65
Number of Cells or Batteries		1 - 2	1 - 2	1 - 2	1	1	2
Cell or Battery Type		10 DK	20 DK	60 DK	TR 7/8	4/100 DKO	150 RS

Fig. 9/53:
Circuit diagram of a socket charger for two button cells (nominal constant current = W-characteristic)
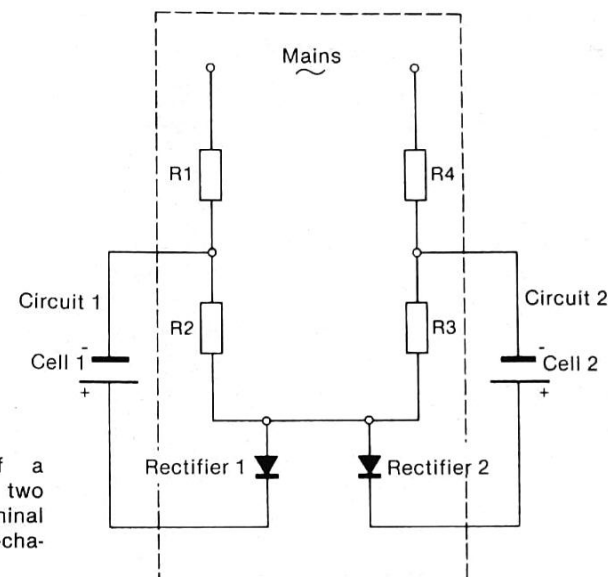
Fig. 9/54:
Circuit diagram of a socket charger for a single button cell battery (nominal constant current = W-characteristic)
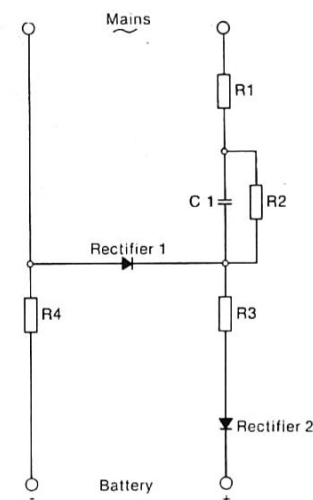
As can be seen in the circuits in Figs. 9/53 and 9/54, the charging current is controlled by resistors (combinations of resistors and capacitors can also be used) and the countervoltage of the cells under charge. These circuits, therefore, have nominal constant current (W-)characteristics. The initial charging current on connection to 220 V/50 Hz mains is 1.2 times the nominal charging current (0.12 C_{10}A), and the final charging current is 0.08 C_{10}A. Charging

should be disconnected after 14 hours. If the unit is connected to 110 V/50 Hz mains, the charging current will be halved, and the charging period has to be increased to 28 hours.

When charging is completed, the batteries should be removed from the charger in order to avoid discharge back through the diodes (reverse current).

9.4.3.3 Universal Chargers — For all Sealed Cells and Batteries

VARTA universal chargers have already been described in section 9.4.2. They are chargers with nominal (W-) or full constant current (I-)characteristics to which 1—10 and 1—20 cells can be connected at will, and which will accomodate cells of different capacities. VARTA also supplies cell holders suitable for cells type 501 RS, RSH 1.8 and RSH 4, and the necessary connecting leads (Figs. 9/55 and 9/56 and Table 9/12). Because there must be electrical isolation from the mains, all universal chargers include isolating transformers (Table 9/11).
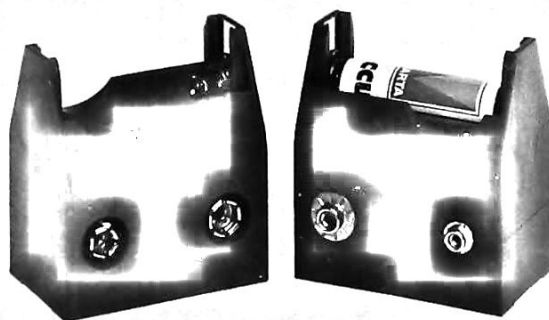
Fig. 9/55:
Cell holders for type 501 RS cells
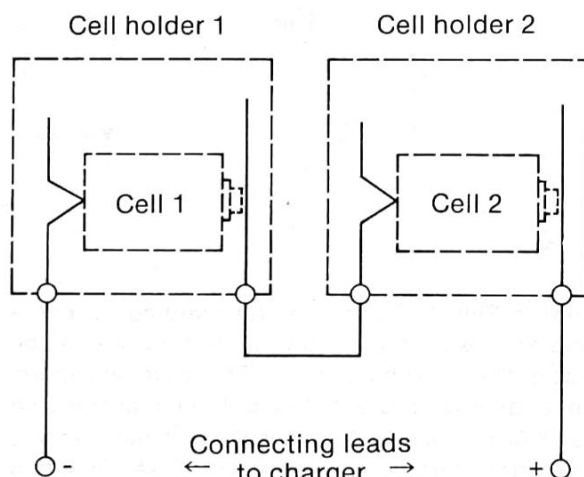
Fig. 9/56:
Block diagram showing cell holder circuit

Table 9/11:
Universal Chargers

Type	Uni I	Uni II	Uni III	Uni III	Multi-Charger	Uni IV
Type Number	GE 1.2-12/ 0.005-0.1 ekx	GE 1.2-12/ 0.1-0.5 ekx	GE 1.2-12/ 0.09-0.75 ex	GE 1.2-12/ 0.09-0.75 ewx	GE 1.2-12/ 0.012-0.7 krtx	GE 1.2-24/ 0.1-3 hktwx
Remarks	—	—	—	With Time-Switch	With pre-set charging currents	With Time-Switch
Charging Current, max. (mA)	100	500	750	750	700	3000
Current Range (mA)	5-100	100-500	90-750	90-750	12-700	100-3000
A.C. Mains Voltage/50 Hz	220 V	220 V	220 V	220 V	220 V	220 V
Dimensions (mm) Length x Width x Height	115x70x50	160x90x80	100x170x115	100x170x115	160x90x75	205x265x140
Weight (g)	450	900	1800	1800	1000	8000
Number of Cells	1-10	1-10	1-10	1-10	1-5/6-10	1-20
Maximum Cell Capacity for Nominal Charging Rate (Ah)	1	5	7.5	7.5	7	30

Fig. 9/57:
VARTA charger Uni I. Uni II is of similar design

Fig. 9/58:
Circuit of a universal charger with constant current characteristic (ekx), e.g. Uni I

For Cell Type	501 RS	RSH 1.8	RSH 4
Material Colour Dimensions (mm) LxWxH Weight (g)	Polystyrene Blue 61x38x65 45	Polystyrene Blue 60x38x65 45	Polystyrene Blue 73x38x65 47
Connecting Leads 1	For use in conjunction with cell-holders listed above or with batteries having large press-stud contacts, joining to uni- and multi-chargers.		
Connecting Leads 2	For use with uni- and multi-chargers, for connecting to battery type TR 7/8, or to other batteries with small press-stud contacts.		
Connecting Leads 3	For use with uni- and multi-chargers, for connecting to rectangular cells/batteries, or to batteries with other than press-stud contacts.		
Connecting Leads Length	Charging Leads 1 - 3		
	Approx. 1.5 m		
Conductor Cross-Section	2×0.75 mm^2		
Polarity	Plus (+) = Red Minus (—) = Black		

Figs. 9/57 and 9/59 show two typical models of VARTA Uni-chargers, and Table 9/11 gives the technical specifications. Two examples of the circuits used in these chargers are given in Figs. 9/58 and 9/60. The first is used in the Uni I charger and provides charging on a continuously adjustable constant current I-characteristic (ekx), the second shows the circuit of the Uni III charger which has a continuously adjustable nominal constant current W-characteristic (ex). The Uni II charger, which is similar to Uni I, also has the same regulation of currents and control characteristics as the latter, but in an adjoining range.

Universal charger, Uni IV, includes an important circuit which enables up to 20 cells to be charged; at the end of a pre-set charging period it automatically changes over to a low rate trickle charge.

The adjustment of charging rates for all universal chargers has already been described in section 9.4.2.

9.4.3.4 Multi-Charger — Unit with Pre-set Charging Rates
In the multi-charger with constant current I-characteristic, the most commonly used charging rates are obtained via fixed resistors in the circuit, and are selected from sockets at the panel. There is a choice of the following currents: 12 mA, 50 mA, 120 mA, 200 mA, 450 mA and 700 mA. The unit is shown in Fig. 9/61. The currents selected are maintained to within ± 10% accuracy.

The time limited switching off after normal charging is either manual, or by means of an externally connected time-switch.

9.4.3.5 "Chargebox" — Normal Charging of RS Cells in Socket Chargers with Integrated Holders

These units can charge from 1 to 4 cells that are interchangeable with dry batteries of similar voltage. They include:

— Cell 180 RS (AAA size)   — Cell RSH 1.8 (C size)
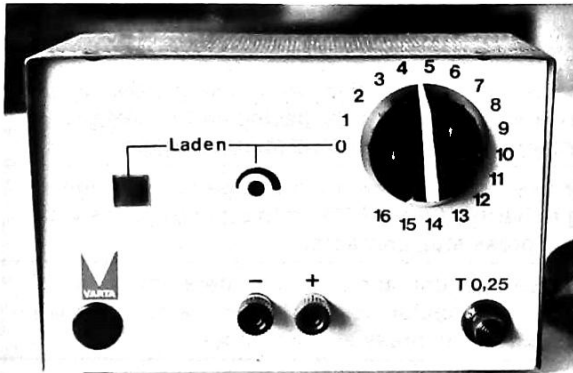— Cell 501 RS (AA size)   — Cell RSH 4 (D size)

Fig. 9/59:
VARTA charger Uni III. Uni IV has similar construction
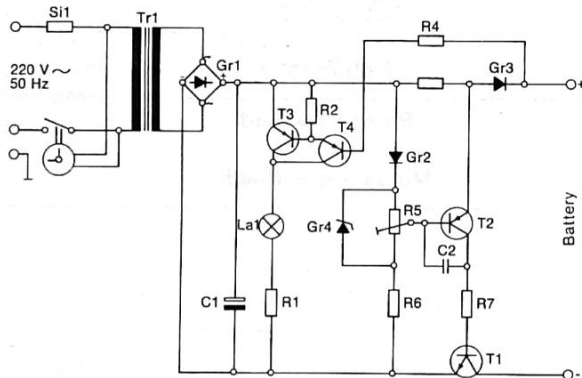

Fig. 9/60:
Circuit of nominal constant current universal charger, e.g. Uni III

The "Chargebox" units for these cells are listed in Table 9/13. Fig. 9/62 shows a "Chargebox" for 1—4 cells, type 501 RS. Their operation is similar to socket chargers, but care is needed to ensure that they are inserted in the correct polarity, otherwise neither charge nor discharge will occur. The cell selection switch is set to the number of cells to be charged, and the charge is initiated by simply plugging into the mains supply (220—240 V, 50 Hz).

Because the cells are connected externally, the circuits must be insulated from the mains; this is achieved by incorporating a transformer as shown in Fig. 9/63. These chargers work on a nominal constant current, and, therefore,

give an initial charging rate of 0.12 CA and end-of-charge current of 0.08 CA. For normal charging, the charger is switched off manually after 14 hours. For charging from an unknown state of discharge, a charging time of 12 hours is sufficient.
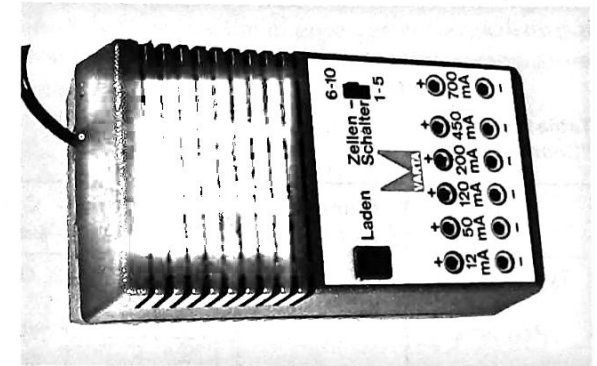
Fig. 9/61:
VARTA Multi-charger. Unit has a pre-selected constant current charge output
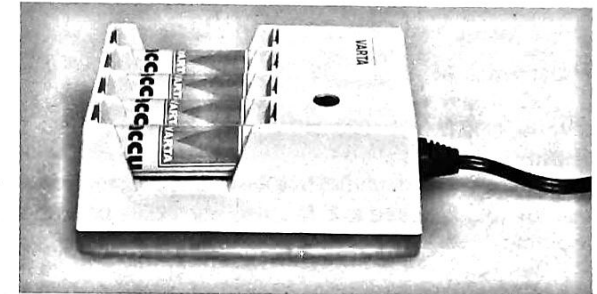
Fig. 9/62:
VARTA ,,Chargebox" for charging 1 to 4 cells type 501 RS. Other "chargebox" units are of similar design
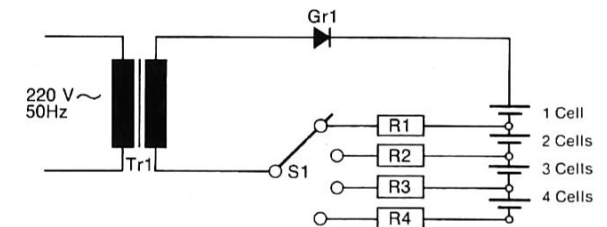
Fig. 9/63:
"Chargebox" charging circuit with a nominal constant current, e.g. 1—4 x 501 RS

9.4.4 Circuits and Units for Fast Charge

9.4.4.1 Fast Charge without Voltage Rise Cut-off

All universal and multi-chargers (sections 9.4.3.3 and 9.4.3.4) can be used for this charging process, when combined with a time-switch.

9.4.4.2 Fast Charge with Voltage Rise Cut-off

Universal and multi-chargers can be used for fast charging only in conjunction with accessory units which will switch off the charge at the cut-off voltage or reduce the charge to a recommended current for the rest of the charging period. This can be achieved with a voltage sensor coupled to a voltage-controlled switch, or electronic discriminator with a similar switching device.

Table 9/13:
"Chargebox" types

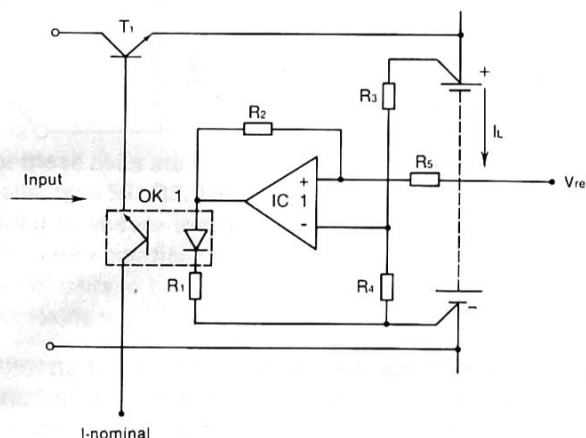| Type	Chargebox 1-4 x 180 RS	Chargebox 1-4 x 501 RS	Chargebox 1-4 x RSH 1.8	Chargebox 1-2 x RSH 4
Type Number	GE 1.2-4.8/ 0.018 x	GE 1.2-4.8/ 0.05 x	GE 1.2-4.8/ 0.18 x	GE 1.2-2.4/ 0.40 x
Remarks		VDE Tested	VDE Tested cell number switch not necessary	VDE Tested cell number switch not necessary
Charging Current (mA)	18	50	180	400
A.C. Mains Voltage/50 Hz	220/240 V	220/240 V	220/240 V	220/240 V
Dimensions LxWxH (mm)	110x75x40	110x75x40	175x67x53	143x78x58
Weight (g)	275	275	580	510
Number of Cells	1 - 4	1 - 4	1 - 4	1 - 2
Cell Type	180 RS	501 RS	RS 1.8; RSH 1.8	RS 4; RSH 4

Fig. 9/64:
Voltage discriminator circuit for fast charge switching without temperature compensation

Fig. 9/64 gives the circuit of a suitable discriminator which is often used in fast charging units. If it is to effect a sharp cut-off (Ia-characteristics), it can be used with a series transistor (series current regulator) to control a constant current charge; alternatively, it can be used with a circuit to reduce the charging current to a safe level (I0Ia-characteristics). The discriminator can incorporate a negative voltage characteristic when related to temperature. Fig. 9/65 shows a circuit which will reduce the charge current when the trip voltage is reached, as detailed in Fig. 9/37. The thermistor temperature sensor is attached to the warmest accessible part of the battery.
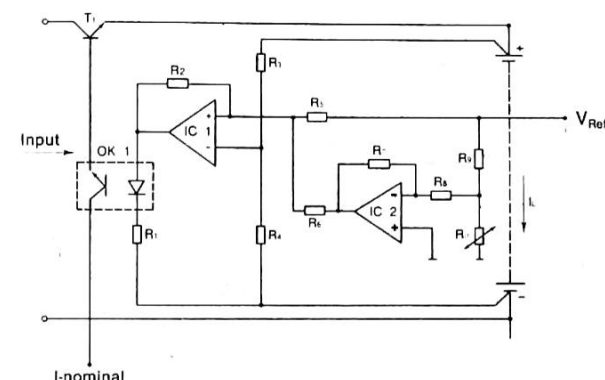
Fig. 9/65:
Voltage discriminator circuit for fast charge switching with temperature compensation

9.4.4.3 Fast Charge by VARTA TSL Method

In this method, a form of pulse charging is used which is particularly suitable for charging large sealed sintered electrode cells, and is based on a modified nominal constant current W0Wa-characteristic.

The special feature of the TSL method is that in the fast charge mode the battery gets nearer to the fully charged state than can be attained with other fast charge methods. This is possible because the battery voltage cut-off signal is not sensed during the pulse or charge current, but is detected between pulses. The system eliminates the voltage peaks clearly visible in Fig. 9/46 and the ohmic voltage drop which are not a true indication of the state of charge and which lead to early tripping.

Fig. 9/66 gives the circuit used in the TSL charger. The charge control thyristor Th 1 is activated via R_2 and closes the circuit supplying the D.C. (100 Hz pulses) to the battery.

The fast charge mode is terminated and the changeover to trickle charge is initiated by the discriminator, which controls the inhibiting of the thyristor. The discriminator compares the battery voltage with a pre-set reference voltage (cut-off voltage) and operates when the two are equal (battery voltage sensed in period between pulses). Fig. 9/67 shows these voltage relationships.

The discriminator reference voltage has approximately the same negative temperature co-efficient as the battery under charge, obtained by using a thermistor with a matching co-efficient to the cell.
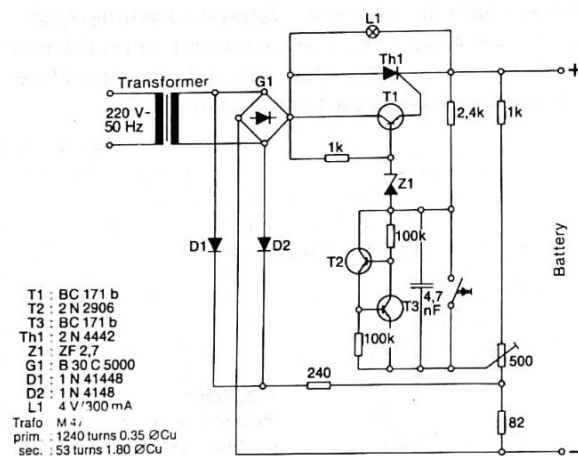

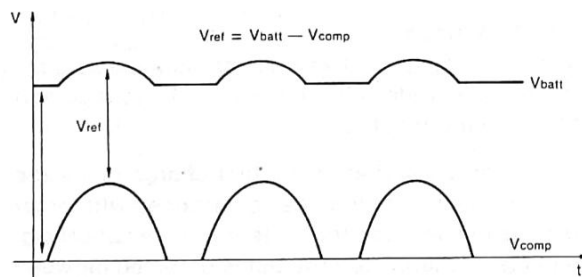
Fig. 9/66:
TSL charger circuit

T1	: BC 171 b
T2	: 2 N 2906
T3	: BC 171 b
Th1	: 2 N 4442
Z1	: ZF 2,7
G1	: B 30 C 5000
D1	: 1 N 41448
D2	: 1 N 4148
L1	4 V/300 mA

Trafo M 4/
prim. : 1240 turns 0.35 ∅Cu
sec. : 53 turns 1.80 ∅Cu

$V_{ref} = V_{batt} - V_{comp}$

Fig. 9/67:
Derivation of reference voltage during TSL charge

9.4.5 Circuits and Units for the VARTA TGI-Charge

The TGI charging method, as already mentioned in section 9.3.5.4, cannot be classified with any of the charging methods described in the above sections. At low temperatures, it is a relatively slow charge, but at high temperatures it is more like the fast charge method. In both cases, it achieves a partial charge which approaches the full charge state. Because self-discharge is temperature dependent and the TGI-charge takes this into account, it is appropriate to pulse charge in the main charging phase, as applies in a simpler way with intermittent charging (section 9.3.7.3). In this way, the full charge state is reached after the partial charge during the first charging phase.

TGI charging circuits consist of a regulator and a control section, forming the basic unit, together with a power section (Fig. 9/68). The power section can be obtained by many methods, i.e. a unit which supplies a D.C. current, or pulses of current and which can be adjusted to suit the voltage and capacity of the battery to be charged.
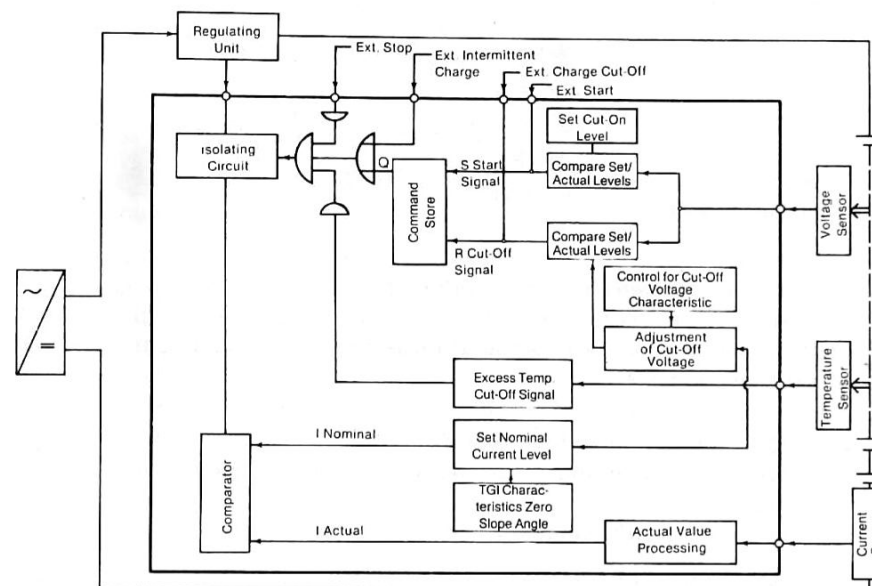
Fig. 9/68:
Block diagram of a TGI Charger

The basic TGI charging unit developed by VARTA is constructed on a printed circuit module (Europaformat) as shown in Fig. 9/69 and includes all the necessary functions ranging from simple charging circuits to those required for general purpose standby power supplies. The various sections can be considered as optional; if they are not all required, the module is equipped correspondingly.

The circuit block diagram given in Fig. 9/68 includes only the basic operations of the TGI system. They are:

1. Automatic control of a constant current charger with charging current regulated by cell temperature.
2. Automatic transmission of a cut-off command signal as soon as the voltage of a battery on charge reaches a pre-set level related to cell temperature.
3. Automatic processing of a command for switching on TGI current when cell voltage falls below a pre-set level.

4. Automatic transmission of a cut-off signal as soon as an upper temperature level is reached and a cut-on signal for a lower temperature level.

Fig. 9/69:
Europaformat module

The basic functions can be varied by adjusting as follows:

1. Alteration of the TGI zero point (temperature at which the charging current is zero) for higher or lower temperature settings and adjustment of the TGI slope angle (Fig. 9/42).
2. Adjustment of the slope of the cut-off characteristic $V_{off} = f(\vartheta)$.
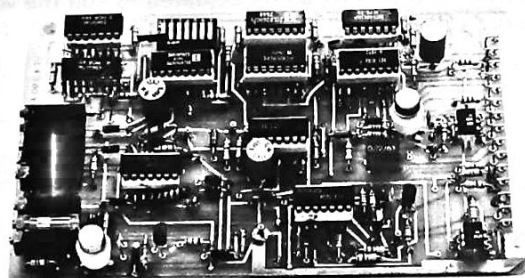3. Setting of the cut-on voltage related to the type of operation concerned (e.g. for simple charging purposes, or for uninterrupted power supply operation).
4. Reduction of the switching differential signal to about 1 °C.

The following functions are also provided on the TGI module shown in Fig. 9/69:

5. Provision of a start- and stop-signal for the TGI-charge. This permits the constant current charger to be set to operate for a limited time to give a charging current related to cell temperature. This can, for example, be performed by a time-switch to carry out intermittent trickle charging.
6. Provision of a changeover command signal to change from TGI-charge to intermittent charge and back again. The automatic action of the time-switch mentioned can be overridden.
7. Provision of a changeover signal to switch on one of two pre-set TGI slope angles (α1 or α2) with the zero point kept constant. With this, for example, for lower temperatures there can be an initial fast charge step, and then after the tripping voltage is reached, the charge can be continued at the optimum current until the cut-off voltage is reached. This sequence can be performed automatically.
8. Provision of a stop signal generated by an external safety circuit. This can consist of a number of monitoring devices connected in series, for example, thermostats, pressure monitors.
9. Self-acting transmission of the intermittent charge signal after item 5 above by an electronic timer mounted on the TGI module, which can also provide time control as required for (5.) above, and be overridden in the way mentioned in (6.). In one model this electronic timer is controlled with a 50Hz input and provides for intermittent charging for 1 hour in 1 minute steps by means of a coding circuit.
10. Provision of a cut-off signal when a lower limit of battery voltage has been passed.
11. Summary of the varieties of the TGI-charge control variables derived from the battery:
    — TGI charging method
    — Trickle charge (e.g. intermittent charging)
    — Excess temperature
    — Lower voltage limit
    — Charging control signal which operates both during charge and discharge whenever a command for constant current charge occurs.

The above shows that the TGI control module shown in Fig. 9/69 can perform all the necessary regulating and control functions which apply to emergency standby power installations.

9.5 Standby Power Supply Systems with Sealed Nickel Cadmium Batteries

9.5.1 Introduction to Types of Battery Operation (VDE 0510)

The simplest system is *purely battery operation* (section 5.6.1 and Fig. 5/68), by which the load is supplied from a battery which is disconnected from the load when ready for recharge. If the load has to have a continuous supply of power then another battery is substituted for the one on charge.

This simple system is not used by itself in emergency power supplies, but more often the *"hybrid" system* is operated, by which the load is supplied both from a power supply (generator, rectifier, mains), and from a battery. This type of operation can be performed in several ways: parallel operation (buffer operation, standby parallel operation), or changeover operation, or parallel operation alternating with battery operation. The common feature of these different forms is that the batteries are only temporarily supplying the load with power.

9.5.2 Hybrid Operation

9.5.2.1 Parallel Operation

In parallel operation, the load, the power supply and the battery are all permanently connected in parallel (Fig. 5/70). Hence, the voltage regulating devices can be connected to the load.

Several different types of battery service are possible for parallel operation:

1. Buffer Operation

The battery is alternately supplying the load or being charged. Its voltage varies correspondingly. The full battery capacity cannot always be available during discharge.

Peak load buffer operation covers the short term peak loads, during which time the battery is not expected to provide its total capacity so much as high current to back up the regular supply. After the peak load demand has passed the battery is immediately charged and is ready to meet the next peak demand.

With *continuous buffer operation*, e.g. for signalling, clock and telecommunications installations, the system consists of trickle charging (section 9.3.4.1).
Voltage stabilizing buffer operation is used when the load varies, in order to keep the voltage of the supply within acceptable limits.

2. Standby Parallel Operation

When the standby power supply system is designed to supply all the loads required, it can be called a standby power supply in the strict sense. The batteries take over when the generator fails — as with buffer operation — and automatically supply the whole of the load demanded. As long as the normal power supply is working satisfactorily, the batteries will be on charge for as long as is necessary to maintain them in the fully charged condition (trickle charge, section 9.3.6).

A typical application of standby parallel operation is for the maintenance of uninterrupted D.C. supplies (UGV), e.g. for process controllers.

9.5.2.2 Changeover Operation (Switch Tripping)

In changeover operation, the lead is continuously supplied by the generator, whilst the battery is disconnected from the load and charged via a separate power supply and subsequently trickle charged. In the event of mains failure, the load is switched over to the battery by a changeover switch or electronic switching circuit (Fig. 5/69). This type of supply is, for example, used in emergency lighting systems. The short period of interruption of supply during changeover from mains to standby supply can be tolerated for these purposes.

Changeover without interruption is a system which is, for example, used for the power supplies of telecommunications installations with D.C. supplies conforming to VDE Standard 0800. The loads connected are continuously supplied from a constant voltage unit. The battery section is usually in two parts, main cells and regulator cells to boost the voltage if necessary, and is connected so that if there is mains failure, the batteries quickly take on the load without a period of interruption (section 9.3.5.1).

9.5.2.3 Parallel Operation Alternating With Battery Operation

In this system, the load and the battery are permanently connected to each other. During periods when the power supply cannot supply sufficient voltage, or is cut off, the supply to the load is maintained by the battery exclusively. The power supply is not reconnected until its voltage exceeds that of the battery. Hence, the battery alternates between supplying the load and being charged.

This type of operation is, for example, found in motor vehicles and in train lighting systems fed from axle generators.
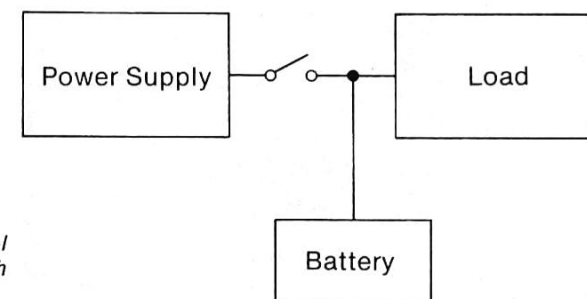
Fig. 9/70:
Block diagram of parallel operation alternating with battery operation

9.5.3 Examples of Circuits and Chargers for Hybrid Operation

9.5.3.1 Parallel Operation
1. Buffer Operation

Systems dependent on mains D.C. supplies and sealed nickel cadmium batteries as buffer batteries are seldom used to maintain a constant voltage supply or for meeting peak load due to varying outside the required tolerance band in battery voltage.

The method is, however, often used for uninterrupted buffer operation, i.e. trickle charging.

A typical example is the supply of power to semiconductor circuits, for example, in more recent television equipment designs (memory back-up). Fig. 9/71 shows a module for such equipment supplied from a type 2/100 DKO. The battery is kept on trickle charge at $0.01C_{10}A$ and the current drain of the load is in the μA region.

Fig. 9/71:
Module with battery type 2/100 DKO power supply caps for TV memory back-up

Fig. 9/72:
Different Primary Energy Conversion Processes
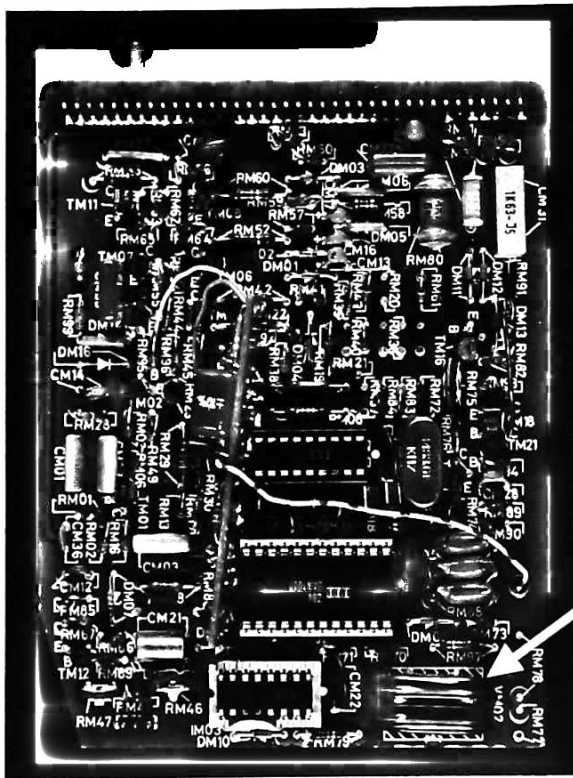
Table 9/14:
Applications of solar-electric power supplies using sealed nickel cadmium batteries

Load Range	Applications
1. µW Range	Small devices: e.g. solar-powered watches and calculators, C-MOS micro-electronics
2. mW Range	— portable power supplies and telecommunications electronics and other low power devices — low power stationary machines such as: ticket machines, bottled drinks machines, money-changers, fire alarms, burglar alarms

Mains-independent hybrid systems, in which sealed nickel cadmium batteries are used in buffer operation are often used. In these, the power supply can, on grounds of economy, not be used for the peak demand, or is only occasionally used to supply the peak current. Fig. 9/72 summarizes the possible processes by which various sources of primary energy (fuels, atomic and solar energy) can be converted into electrical energy. They include direct energy conversion (fuel cells, nuclear cells, solar cells), and also indirect conversion (thermoelectric generators, diesel generators), and represent the most interesting possibilities for mains-independent hybrid systems involving sealed nickel cadmium batteries. In recent years, there has been an interest in other primary energy supplies not included in Fig. 9/72, which may become of practical use in the future. Wind and wave energy can be included in this group.
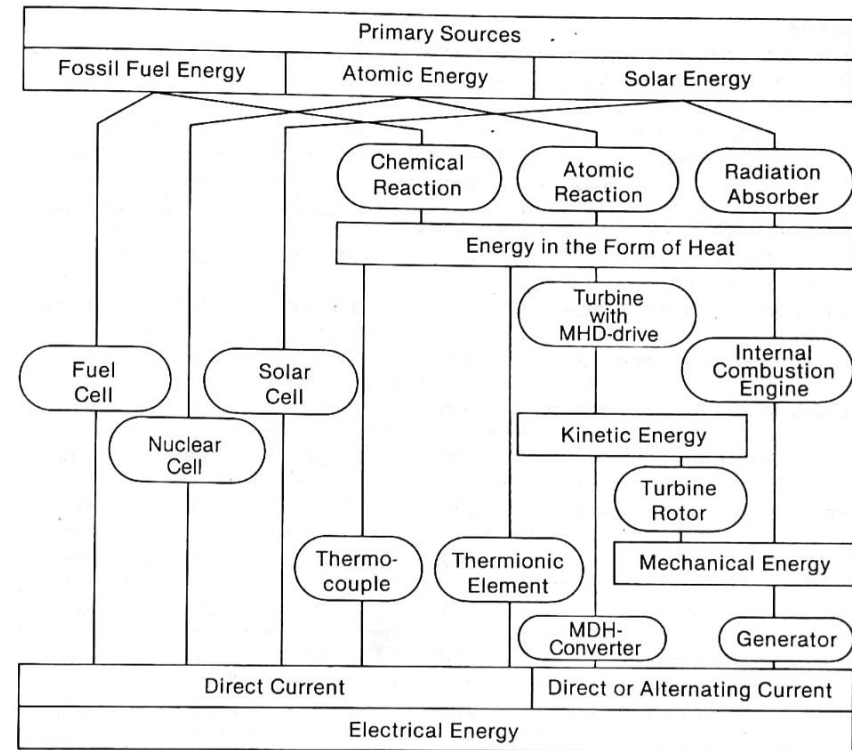
Table 9/15:
Theoretically attainable figures and actually obtained values for sealed nickel cadmium batteries in solar-electric power supplies

Performance Criterion	µW Range Theoretical	Actual (DK, DKZ)	mW Range Theoretical	Actual (RS, SD)
Capacity (Ah)	< 1	0.01 ÷ 1	< 50	50
Full Cycles (up to 80% C nom.)	100	300 ÷ 500	> 2000	< 1000
Maintenance-Free Period (Years)	10	6	> 1	10
Storage Period Possible (Years)	> 5	> 5	> 5	> 5
Reliability (%)	> 99	> 99	> 99	> 99
Deep Discharge Performance (%)	100	100	100	100
Safe Tilting (° ⚡)	180	180	180	180
Sealing (%)	100	100	100	100
Ah-Efficiency (%)	> 95	> 95	> 95	> 87
Minimum Charging Current	0.01CA	0.03CA	0.01CA	0.03CA
Average Self-Discharge (%/Month)	< 1	ca. 15	< 5	ca. 40
Minimum Charging Time (h)	5	10	1	0.5
Trickle Charge Current	0.1CA	0.01CA	0.1CA	0.05CA

The usefulness of these mains-independent hybrid systems is essential for power supplies in generally inaccessible regions, or in temporary installations where connection to the electricity supply grid would not be economical. Among these are included installations for ocean, space and military technology, also power supplies for many civilian purposes as listed in Table 9/14, which are suited to solar-electric power.

Table 9/15 shows the extent of the operational requirements placed on the battery in such power supplies, and the ability of VARTA sealed nickel cadmium batteries to meet such demands.
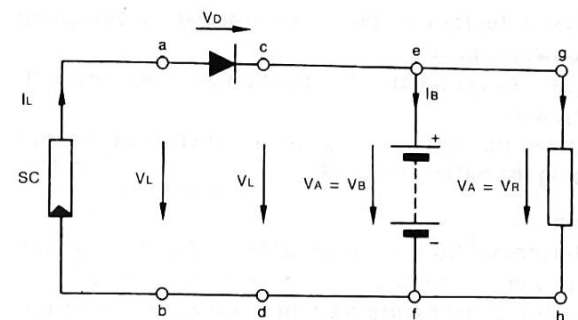
Fig. 9/73:
Basic circuit of a solar-electric power supply without current control
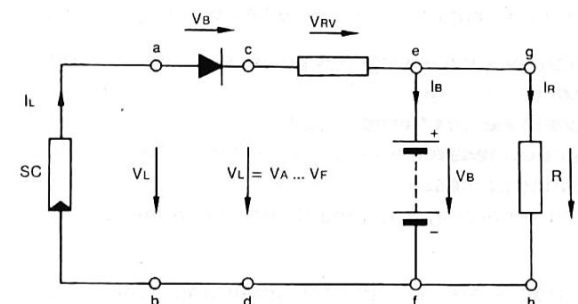
Fig. 9/74:
Basic circuit of a solar-electric power supply with current control
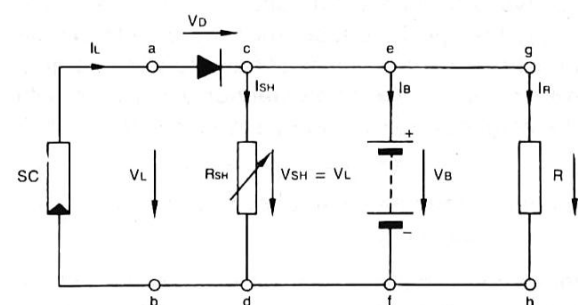
Fig. 9/75:
Basic circuit of a solar-electric power supply with charging voltage and current control

Because solar-electric power supplies have recently become of considerable importance, due to the much reduced price of the solar cell, the basic circuits for these systems are given in Fig. 9/73 to 9/75. The unregulated system can only be used when the solar cell current is available under radiation conditions and over a long period can be taken from the battery without the recommended charging voltage being exceeded. Because this criterion is not normally realized in practice, the other circuits are preferred on the grounds of reliability. The current controlled circuit given in Fig. 9/74 is suitable for watches and pocket calculators; the one in Fig. 9/75 with regulated charging voltage and current (shunt regulator) in various forms is used for the great variety of other circuits listed in Table 9/14.

Generally there are two major factors to be considered while designing hybrid mains-independent power supplies:
— the current generator must always be able to maintain the charging voltage needed by the battery, and
— in the worst case, the generator current must be at least equal to that required for trickle charging the battery (Table 9/6).

2. Standby Parallel Operation

A typical example here is the installation of sealed nickel cadmium batteries for stationary emergency power supplies which can maintain an uninterrupted D.C. supply in the event of deliberate switching off or failure of the mains (UGV-sets; USV-sets for A.C. supplies) for limited emergency periods.

Important fields of application for such emergency power supplies include:
— Warning signs, fire alarms
— Electronic data processors in various forms
— Cash registers and similar business machines
— Controllers for manufacturing processes
— Electronic controllers and recording equipment for telephone systems, radio and television.

Cells with mass plate electrodes are suitable for small and average size loads, and sintered electrode types for heavy duty applications. If a single battery assembly cannot supply the specified load, then more units can be coupled in parallel; when this is done, each group must have its own charging circuit with provision to prevent reverse current flow (section 9.3.7). Figs. 9/49 and 9/50 show the design of emergency power supply systems with multiple battery banks.

As an alternative to this solution, complete emergency power supply units can be operated in parallel to give greater capacity.

The type of switching and the circuits employed are governed by the voltage limits to be maintained for charge and discharge during mains failure (section 9.2.1).

For a greater factor of safety, the end-of-discharge voltage can be specified as higher than that quoted (normally 1.0V per cell). During fast charge, the charging voltage can be raised to a cut-off level of 1.6V (Fig. 9/37).

If voltage stability of $\pm 20\%$ is sufficient, compared to the nominal voltage, and if the load current is average, then the trickle charging circuit shown in Fig. 9/76 can be used. Because button cells can be charged continuously at a maximum of 0.01CA and sintered cells at 0.05CA, much lower currents are sufficient to maintain the battery capacity and a larger fraction of the current is available for supplying the load. If the external load is constant, then the trickle charge current can be increased to this value. The battery takes care of any peak loads required and can also supply the load should the mains fail.

Fig. 9/76: *Circuit diagram of a UGV-set with constant current charger, I-characteristic*
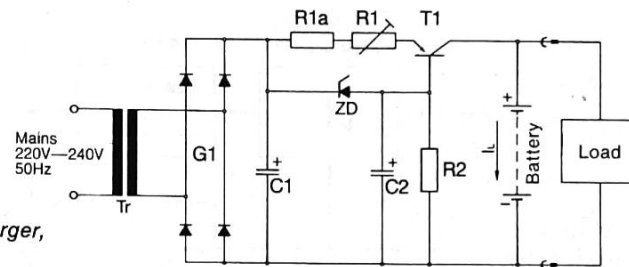
The circuit can be considerably simplified if a load with a nominal voltage of 2.4V or 3.6V has to be supplied with a relatively constant current. It is possible to use a charging circuit as shown in Fig. 9/64, and use the system shown in Fig. 9/77.

Fig. 9/77: *Circuit diagram of a UGV-set with nominal constant current charger, W-characteristic*
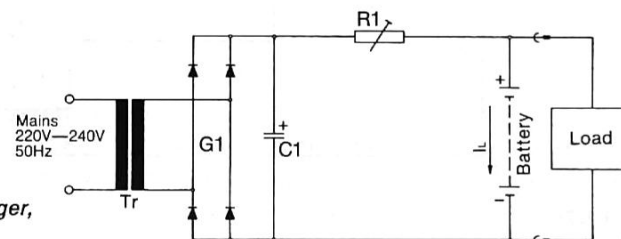
The block diagram given in Fig. 9/78 represents a UGV installation for standby parallel operation designed to work with large rectangular cells. Installations of this kind either have the batteries charged at constant current or by the TGI method, up to the cut-off voltage level, and kept fully charged by trickle charging at pre-set time intervals. With these units, the load is permanently connected to the power supply, which has its voltage regulated so that the battery is charged at the recommended rate. Should the mains fail, the battery automatically supplies the load without interruption. The operation limits of the system are $+25\%$ to -16% of the nominal voltage.

Fig. 9/78:
Block diagram for UGV System

Fig. 9/79:
Block diagram of UGV-set in standby parallel operation with blocking diodes
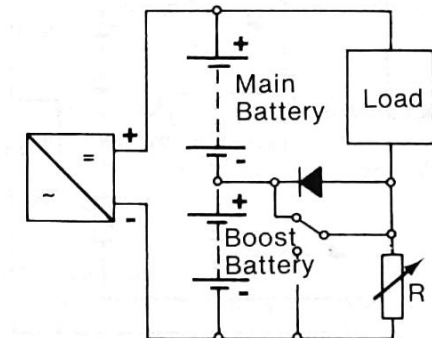
Fig. 9/80:
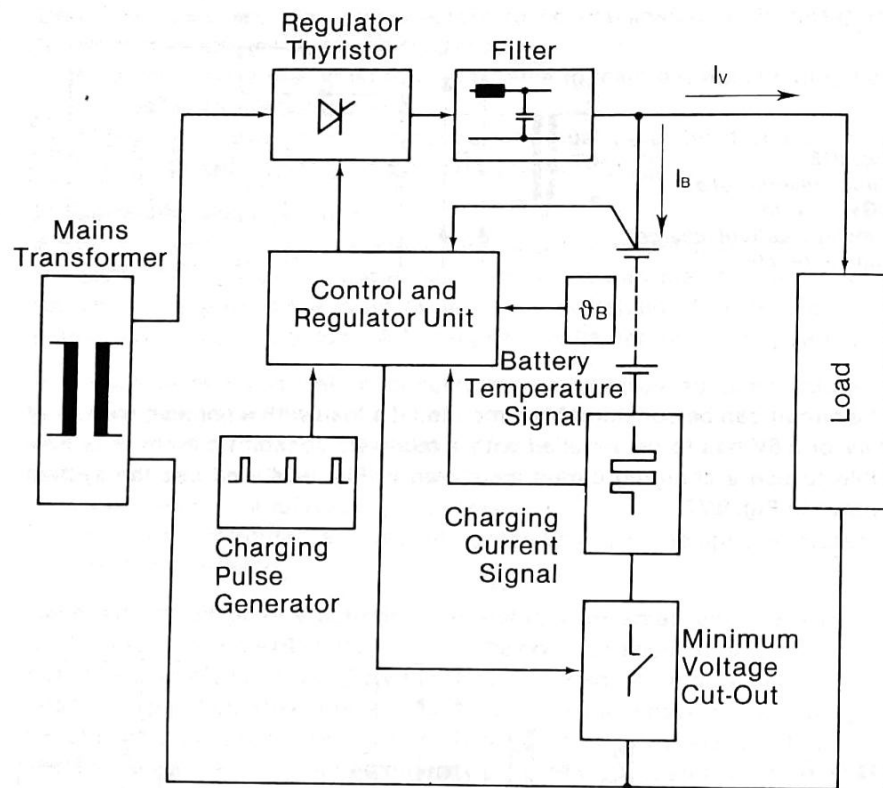*Block diagram of a UGV-set in standby parallel operation with main and boost battery*

9.5.3.2 Changeover Operation

The ordinary form of changeover operation will not be discussed in detail in this section, which deals with the uninterrupted changeover system. The limits which apply here are ± 12% of the nominal voltage. With these systems, it is generally assumed that during normal operation, the D.C. supply is capable of meeting all the load requirements.

If these tolerances are too large for the load then standby parallel operation can only be used when diodes are inserted in the circuit as shown in Fig. 9/79, to block reverser currents; an alternative system is to have the main battery backed up with additional cells as shown in Fig. 9/80. In the first case, the diodes connected before the load compensate for a part of the higher charging voltage and during mains failure block any voltage surge in the discharge direction. In the second case, the load is normally supplied from the main battery; on mains failure, a lower voltage limit is reached and a switch brings in the additional battery. The diode in the circuit prevents a break in the discharge current during the switchover period.
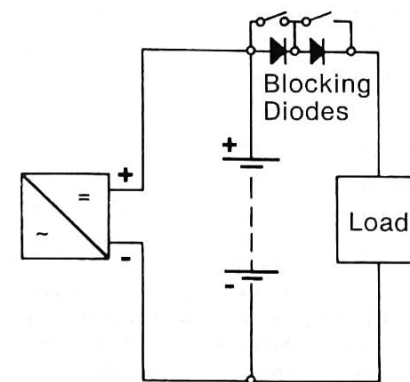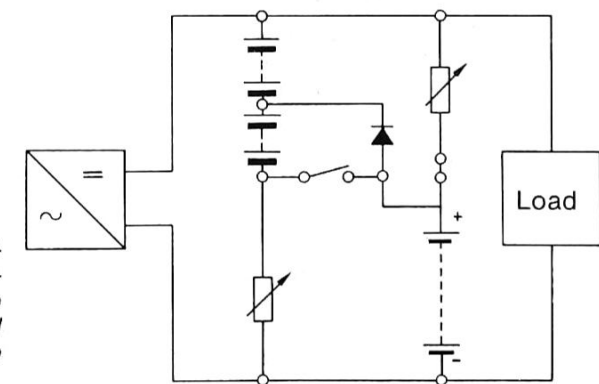

Fig. 9/81:
Block diagram of a UGV-set with two equal batteries and a diode to maintain uninterrupted supply (UGV-set with two battery groups)
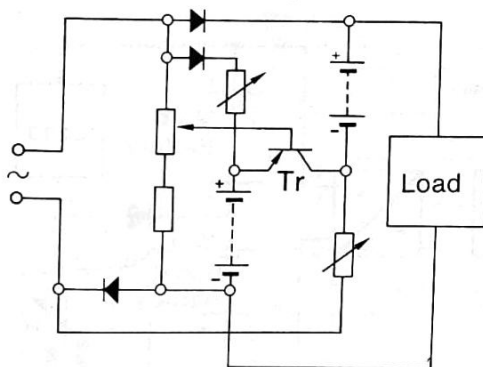
Fig. 9/82:
Block diagram of a UGV-set with electronic battery switch-on (UGV-set with two battery groups)
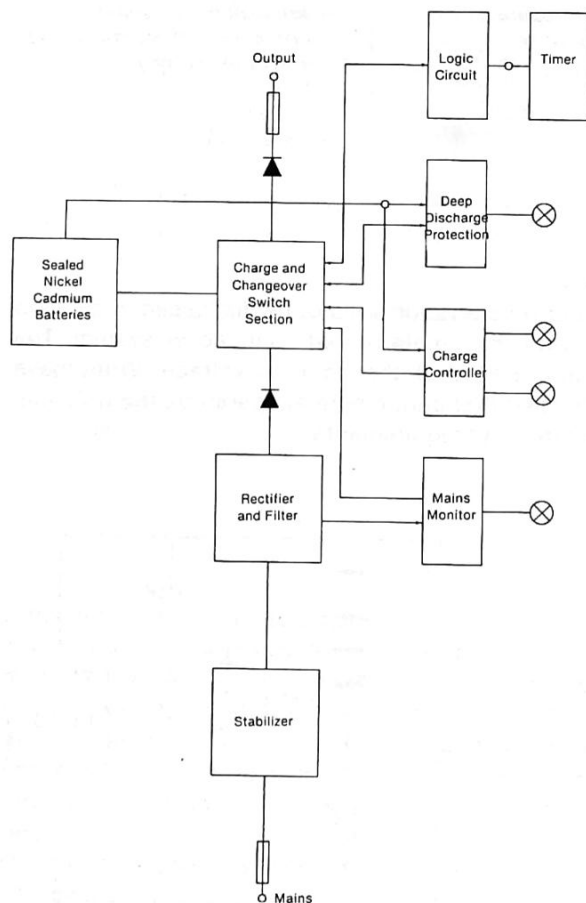
Fig. 9/83:
Block diagram of a typical VARTA UGV-set

The basis of these installations consists of dividing the battery bank into two parts, which, while the mains supply is available, are disconnected from the load and kept on charge (Figs. 9/81 and 9/82).

On mains failure, the groups of cells are immediately switched to supply the load by means of a mechanical switch combined with a diode, or by an electronic switch. In the first case, the diode circuit ensures that the battery can be connected to the supply during normal operation.

Another way of ensuring uninterrupted supply is to isolate the load circuit and the charging current circuit from each other completely and when the battery is required to supply the load, the battery is switched in initially by a fast acting thyristor and then by-passing this afterwards with a switch. This method is used in the VARTA 24V-UGV-set in 19-inch racks. The circuitry is shown in schematic form in Fig. 9/83. This provides automatic insertion of the battery when the mains supply falls 10% below nominal voltage.

This system can be fitted with various rectangular sintered cells, as shown in Table 9/16; the maximum output power is 480W for 0.4 hours at a nominal voltage of 24V. The voltage stability is ±12%. For higher power several of these units can be connected in parallel. Should one of the units fail, say with an internal short circuit, the others will not be affected.

Table 9/16:
Product chart of UGV-sets produced by VARTA

Type	Output Current Permanent (A)	Output Current Temporary (A)	Mains Failure Period (h)	Dimensions (mm) L	Dimensions (mm) H	Dimensions (mm) W	Battery Cell Type	Battery No. of Cells	Total Weight Approx. (kg)
UGV 24/2,5/0,5	2,5	7,5	0,5	483	132	250	SD 1,6	20	14
UGV 24/2,5/1	2,5	7,5	1,0	483	132	250	SD 2,6	20	17
UGV 24/5/0,5	5,0	15	0,5	483	132	250	SD 2,6	20	17
UGV 24/5/1	5,0	15	1,0	483	132	350	SD 7	20	27
UGV 24/10/0,5	10	30	0,5	483	132	450	SD 7	20	27
UGV 24/10/1	10	30	1,0	483	132	450	SD 15	20	45
UGV 24/20/0,4	20	60	0,4	483	177	450	SD 15	20	45

10. Standards and Regulations

10.1 Standardization

Technology is closely involved in following and the setting of standards. This is undertaken by standardization committees and working parties made up from all the circles of specialists involved, who attempt to regulate affairs in the present day world so far as technology is concerned. The basic principles used in the setting of standards are themselves laid down as standard procedure in DIN 820 (Part 1) (34). The standard is defined by a methodical treatment of the topic in matters both material and non-material, bearing in mind the benefit to the public at large. Standards must not create an economical advantage of single parties.

Some generally recognized and obligatory principle forms the basis for every standard. The way in which such principles are defined depends on their individual importance and the object in view. Therefore, one sees standards for measurements, test regulations, standards for the properties of the materials used, or for general levels of quality and performance.

Standards are legal definitions and as such must conform both to the acknowledged principles of technology as well as to established legal terminology, particularly that for contracts and agreements.

For Germany and for West Berlin, the "Deutsche Elektrotechnische Kommission (DKE)" is the national organization for standards and safety regulations over the whole field of electrical technology, and hence has responsibility for primary and secondary batteries in particular.

The results of this process of setting standards are incorporated into the "Deutsche Industrie Norm" $\overline{\text{DIN}}$ which covers manufacturing industry as a whole.

The DKE Organization, with its 120 committees, 200 sub-committees and 400 working parties, is responsible for about 3000 DIN standards and about 350 VDE regulations.

10.2 National and International Standardization and Standards
The standards for the field of electrotechnology in Germany are:
— DIN Standard
— DIN-EN Standards (European Norms — see DIN 820, Part 13)
— DIN-IEC Standards (worldwide standards — see DIN 820, Part 15)
— VDE Regulations (also known as DIN-VDE-Norm)
— VDE Guidelines (also known as DIN-Norm)

As in Germany, there are other national bodies which lay down their own standards and regulations. Some of these are listed below:
— France
NF (Norme française AFNOR = Association Française de Normalisation)
UTE standards (Union Technique de l'Electricité)
— United Kingdom
BS (formerly BSS) (British Standard)
— Japan
JIS (Japanese Industrial Standard)
— USA
ASTM (American Society for Testing of Materials)
MIL, NEMA = National Electrical Manufacturers Association
ISA, and many more.
There are now some wider ranging European standards (EN), and CEN (Comité Européen de Normalisation), and CENEC (Comité Européen de Normalisation Electrotechnique). DIN-EN standards are published in French and English as well as in German.

Beyond these some worldwide standards should be mentioned:
— IEC, International Electrotechnical Commission
— ISO, International Standards Organization
— CEE, International Commission on Rules for the Approval of Electrical Equipment.

10.3 Procedure from Proposal to Specification of Standard

Following DIN 820 (Part 1), any person can initiate the standardization procedure. When the need for a particular standard has been established, a permanent working party is formed to consider the proposals and formulated a discussion paper to serve as a basis for the interested parties. Fig. 10.1 shows schematically the way in which a standard is established following the initial proposal.

For more than three decades, VARTA has participated in the production of German and international standards publications, and has collaborated in establishing standards for primary and secondary batteries.

The experience accumulated by VARTA from its research, development, technology and manufacturing methods flows not only internally into its own works standards, test specifications, working manuals and materials specifications in general, but also in departmental manufacturing instructions, standards and official regulations.

The staff of VARTA also work in honorary capacities in countless national and international working parties which perform the tasks of establishing technical standards. The collaboration of VARTA in this field is set out in Fig. 10/2.

Standards ought not be incompatible with legal and administrative regulations. They also have to take into account the current state of scientific and technological advances and economic factors.

Observance of the guidelines set out in a standard can involve the manufacturer in extra costs and requires changes in production methods. Hence, standards and regulations ought not to be frivolously published, and in order that adequate time is available for industry to adapt to changes, many standards do not come into force until several years have passed after their publication.

Because standards have to be compatible with the current state of technology, they have to be continually checked and adapted to changing circumstances. This procedure is carried out at specified intervals. Whenever serious changes to a standard are necessary, these must be published and consultation procedures followed. These changes may involve a widening in the scope of the standard, in which case the same rules apply as set out in Fig. 10/1.
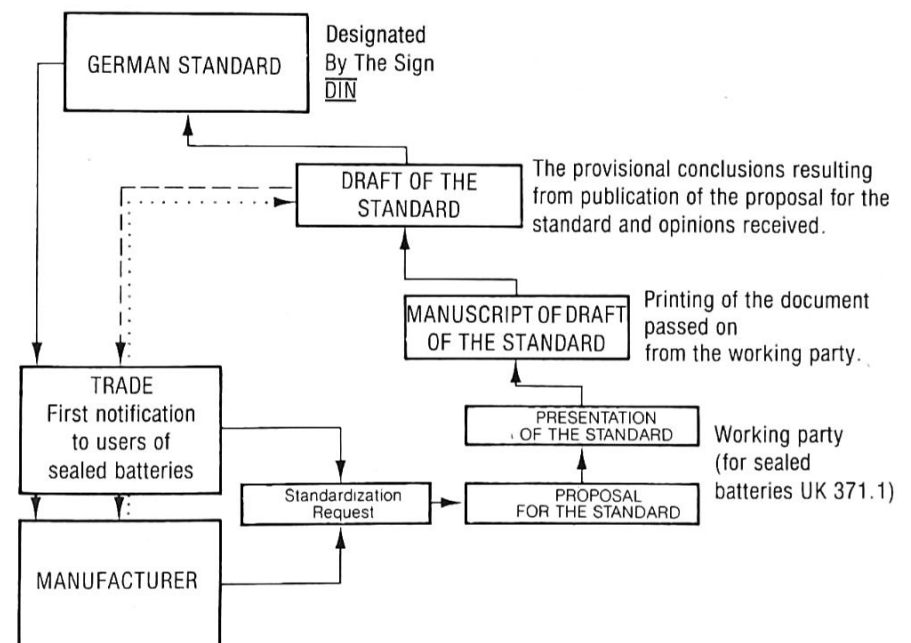

Fig. 10/1:
Schematic diagram of procedure from proposal to publication of standard (to DIN 820, Part 1)
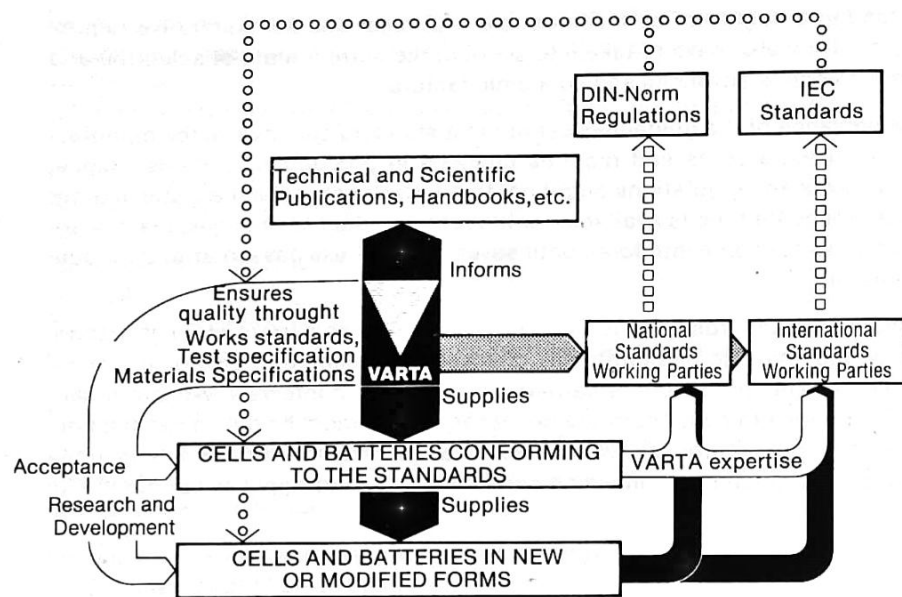
Fig. 10/2:
VARTA involvement in originating standards and regulations

10.4 Dimension Standards

Those dimensions which have over the years become well established in commerce are particularly suitable for standardization. Objects that are in everyday use sell best when they are of a convenient size for handling. A rod or bar can be comfortably gripped when its diameter is between 25mm and 35mm. 25.4mm corresponds to one inch, and it is not surprising that the first primary cell used in hand torches had a diameter corresponding to the inch.

Almost all nickel cadmium batteries have sizes that can be traced back to this 25.4mm dimension. The development of these maintenance free batteries is also related to this dimension, because since their first appearance, they have been manufactured as economical substitutes for primary cells.

Fig. 10/3 reproduces the range in dimensions of the different types of sealed nickel cadmium batteries.
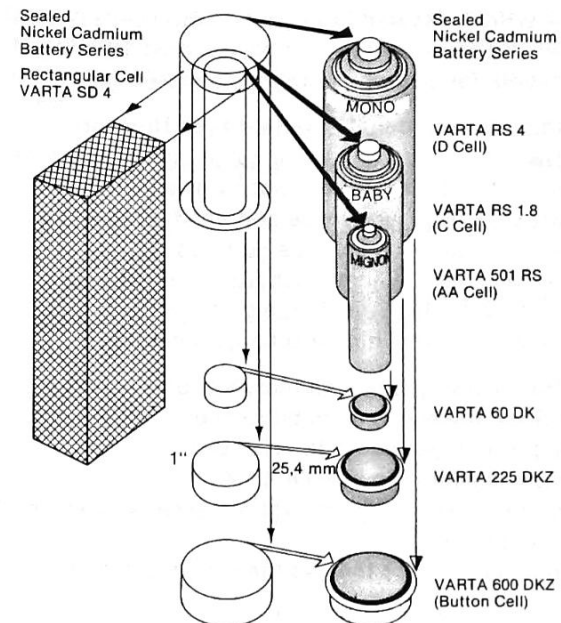
Fig. 10/3:
Summary of sealed nickel cadmium battery dimensions

10.5 Type Specifications and Development of VARTA Sealed Nickel Cadmium Batteries

VARTA supplies sealed nickel cadmium batteries in three different forms:
— Button cells, having a diameter greater than the height; oval cells are in this group.
— Cylindrical cells (also known as round cells).
— Rectangular cells.

As already mentioned, sealed batteries can also be classified according to their type of construction. VARTA manufactures two kinds:
— Cells with mass plate electrodes.
— Cells with sintered electrodes.

To distinguish between the various types of construction, forms and capacities, sealed nickel cadmium batteries are designated by a type number consisting of letters and numerals.

10.5.1 German Standard Type Numbers

Because it is not the usual practice to adopt a firm's type numbers for standard lists, the VARTA equivalents to the German standard types are given below:
— GNK for sealed button cells for normal discharge rates (VARTA: DK)

— GHK for sealed heavy duty button cells (VARTA: DKZ)
— GSZ for sealed cylindrical sintered cells (VARTA: RS)
— GSP for sealed rectangular sintered cells (VARTA: SD)

10.5.2 International Standard Type Numbers

The IEC standards, which came later in use than the German standards for sealed batteries, have a discharge specification for nickel cadmium batteries which is used worldwide and which is given by the letters:
— L = for low discharge currents
— M = for medium discharge currents
— H = for high discharge currents
— X = for very high discharge currents

The following are customary symbols used for sealed batteries:
KB for nickel cadmium button cells
e.g. KBL is similar to VARTA: DK
KBM is similar to VARTA: DKZ
KR for nickel cadmium cylindrical cells, in which "R" = "round", was derived from primary cells.
In this case also there is the equivalent: KRH is similar to VARTA: RSH

IEC KR 27/50 (R 14)   IEC R 14

Fig. 10/4:
Example of a sealed nickel cadmium cell physically interchangeable with a primary cell made by VARTA to IEC specifications

National standards have taken over increasingly the IEC specifications so that worldwide interchangeability of the individual primary cell types has become possible. Today VARTA primary and sealed nickel cadmium cells carry the IEC symbols (Fig. 10/4).

10.6 Capacity Comparisons between Rechargeable Nickel Cadmium Batteries and Primary Batteries

For sealed nickel cadmium batteries, the capacity is given in Ah or mAh in relation to the discharge conditions laid down by standard or by the manufacturer. For primary batteries, the standard defines the working life in hours after a specified shelf life, and a stated type of discharge (Fig. 10/5).

Fig. 10/5:
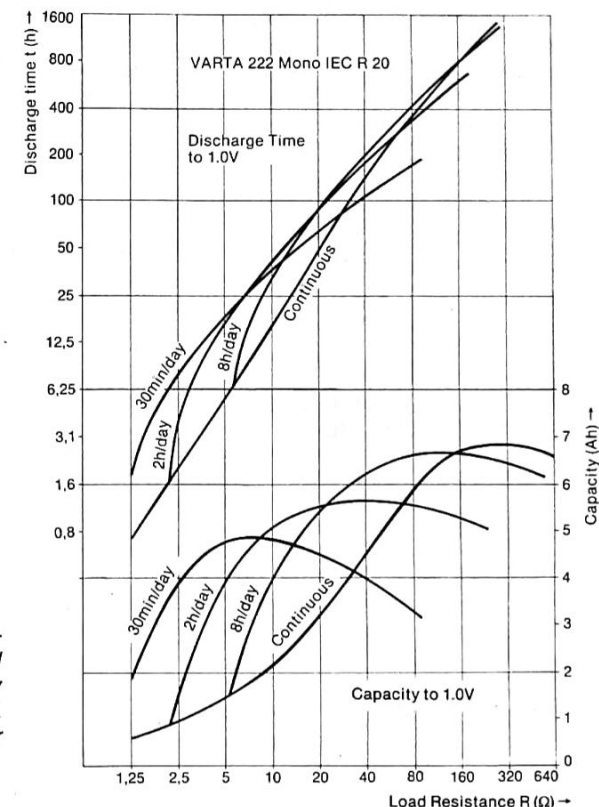*Discharge time and capacity in relation to load resistance of a primary cell (Mono cell VARTA Cat. No. 222, IEC R20) for normal discharge*

Strictly speaking, the storage capacity of secondary and primary cells cannot be compared precisely because for dry batteries the capacity is specified for one discharge only, whereas for rechargeable batteries, it is possible to obtain a large number of charge/discharge cycles.

Hence, the data given in Table 10/1 should be considered as only a broad comparison of some well known cell types.

Table 10/1:
IEC Designation of some sealed nickel cadmium batteries physically interchangeable with primary cells

Primary Cells (Manganese Oxide)	Sealed Nickel Cadmium Batteries
IEC R 20 Mono Cell(D) Approx. 4.8Ah for daily discharge through 5 Ω for 30 min	IEC KR 35/62 e.g. VARTA RSH 4 4Ah for 5 hours to 1.0V/cell
IEC R 14 Baby Cell (C) Approx. 1.9Ah for daily discharge through 5 Ω for 30 min	IEC KR 27/50 e.g. VARTA RSH 1.8 1.8Ah for 5 hours to 1.0V/cell
IEC R 6 Mignon (AA) Approx. 530mAh for daily discharge through 75 Ω for 4 h	IEC KR 15/51 e.g. VARTA 501 RS 500mAh for 5 hours to 1.0V/cell
IEC R 9 Button Cell Approx. 150mAh for daily discharge through 300 Ω for 12 h	IEC KBL 16/7 e.g. VARTA 60 DK 60mAh for 10 hours to 1.1V/cell

10.7 Test Specifications

The characteristic features of a standardized item must be capable of measurement and comparison. Therefore, it is necessary to specify test methods, sequences of tests, duration of tests, etc.

Sealed nickel cadmium batteries are tested in accordance with DIN 40 764 (Part 3) (35). This standard specification complies with IEC Publication 285-1 (30).

DIN 40 764 (Part 3) specifies the most important tests for sealed nickel cadmium batteries, including the 5- and 10-hour capacity tests at 20 °C and —18 °C, for:
— Self-discharge
— Safety against overcharge
— Polarity reversal
— Useful life

Table 10/2:
Summary of the most important standards and regulations applicable to sealed nickel cadmium batteries

Title	Specification
DIN 40 729	Secondary batteries, basic principles
DIN 40 764, Part 3	Nickel cadmium batteries, sealed cells, electrical tests.
DIN 40 765	Nickel cadmium batteries, mass plate button cells, capacities, dimensions, technical specifications.
DIN 40 766	Sealed nickel cadmium batteries with sintered electrodes in cylindrical and rectangular forms, dimensions and technical specifications.
DIN 40 768	Sealed nickel cadmium batteries, 6V and 12V batteries made from mass plate button cells, dimensions and technical specifications.
DIN 41 772	Rectifiers, semiconductor rectifier units, shapes of and brief notes on the characteristics.
Additional Sheet 1	Rectifiers, semiconductor rectifier units and equipment, characteristics for charging units.
Additional Sheet 2	Rectifiers, semiconductor rectifier units, characteristics for equipment used in parallel with batteries.
VDE 0510	VDE regulations for batteries and battery installations.
IEC Publication 285-1	Sealed nickel cadmium cylindrical rechargeable single cells, general requirements and test methods.
285-1A	First supplement.
285-2	Dimensions.
509	Sealed nickel cadmium button rechargeable single cells.
VG 95 212, Part 15	List of accepted electronic and electrical component parts (LZB) secondary batteries.
VG 95 230	Nickel cadmium batteries, sealed, cells and batteries.

In practice, there are naturally far more different applications than a general obligatory standard can emcompass. VARTA can guarantee the required performance of sealed nickel cadmium batteries because they issue works and internal departmental test regulations and after manufacturing, test either 100% production or make random sample tests according to the type of application.

Table 10/2 gives a summary of the most important DIN and VG standards, VDE regulations and IEC publications for the lists and testing of sealed nickel cadmium batteries.

As already described in detail in Chapter 8, at VARTA works there is not only final testing of sealed batteries, but also routine sampling of individual cell components off the production line, and this provides the basis for the high quality of their range of products.

10.8 VDE Regulations

DIN 57 510 and VDE Regulation 0510 (22) apply to batteries and battery installations. Because sealed nickel cadmium batteries are maintenance free, some of the items in these specifications are not applicable. In such cases, the manufacturer's recommendations are to be followed.

11. Bibliography

1) A. Winsel, Sonderdruck Ullmanns Enzyklopädie Bd. 12 Teil 4 (1976). Galvanische Elemente: Brennstoffzellen. (Special Edition of Ullmann's Encyclopaedia, Vol. 12, Part 4 (1976). Voltaic cells: fuel cells.)
2) D. Berndt, Sonderdruck Ullmanns Enzyklopädie Bd. 12 Teil 4 (1976). Galvanische Elemente: Primär- und Sekundärzellen (Special Edition of Ullmann's Encyclopaedia, Vol. 12, Part 4 (1976). Voltaic cells: primary and secondary cells.)
3) A. Dassler, A. E. Lange, E. Langguth, E. Breuning, DRP 674829 (1933).
4) G. Neumann, FP 1004176 (1947).
5) S. U. Falk, A. J. Salkind, Alkaline Storage Batteries.
6) R. Barnard, G. S. Edwards, J. A. Lee, F. L. Tye, "Effects of charge rate and cycling on the morphology of Cd and $Cd(OH_2)$ in sintered plate electrodes". Journal of Applied Electrochemistry 6 (1976), 436.
7) H. F. Gossenberger. "A study of the variables in the Ni-Cd-cell." MCRE Thesis, Polytechnic Institute of Brooklyn, June 1959, p. 11.
8) H. Bode, K. Dehmelt, J. Witte. Electrochimica Acta 11 (1966), 1079.
9) W. Dennstedt, W. Löser. Electrochimica Acta (1971), 429.
10) H. Bode, K. Dehmelt, J. Witte, "Zur Kenntnis der Nickelhydroxid-Elektrode (II). Über die Oxidationsprodukte von Ni-(II)-hydroxiden". Zeitschr. für anorganische u. allgem. Chemie Bd. 366, H. 1 – 2, S. 1 – 21 ("Understanding the nickel hydroxide electrode. The oxidation products of Ni-(II)-hydroxide.")
11) E. J. Casey, A. R. Dubois, P. E. Lake, W. J. Moroz, "Effects of foreign ions on Ni-hydroxide and Cd-electrodes", Journal of Electrochem. Soc., Vol. 112, No. 4, 371 – 383.
12) R. J. Doran, "Impurity effects in metal hydroxide electrodes", Proceedings International Symposium on Batteries 1958, Christchurch.
13) P. Ness, "Quelling pos. Nickelhydroxidmassen und Maßnahmen zu ihrer Verhinderung" (Swelling of positive nickel hydroxide active mass and measures to prevent it). Vortrag auf ISE-Diskussionstagung, Kelkheim 11. 5. 1973.
14) H. Bode, W. Dennstedt, "Zur Kenntnis der Nickelhydroxid-Elektrode (V). Analyse und elektrochemisches Verhalten von Cd-Ni-hydroxiden". (Understanding the nickel hydroxide electrode (V). Analysis and electrochemical behaviour of Cd-Ni-hydroxides). Electrochimica Acta 1972, Vol. 17, 609 – 618.
15) S. Lerner et al., "An investigation of the Ni-oxide electrode", U. S. Department of Commerce, National Bureau of Standards, NASA, No. NAS 3 – 10608.
16) G. Krämer, E. Tisch, P. Ness, "Positive Nickelhydroxid als aktive Masse enthaltende Elektrode für alkalische Akkumulatoren", Offenlegungsschrift Nr. 2340869. (Positive electrodes containing nickel hydroxide for alkaline batteries).
17) B. Hodge, Y. Lecouffe, "Military sealed Ni-Cd-batteries". Power Sources Symposium 1970, Brighton, U. K.

18) P. C. Milner, U. B. Thomas, "Advances in Electrochemistry and Electrochemical Engineering", C. W. Tobia Editor Vol. 5, Interscience Publishers, N. Y. 1967.

19) E. H. Rubin, B. Baboian, "A correlation of the solution properties and the electrochemical behaviour of the nickel hydroxide electrode in binary aqueous alkali hydroxides", J. Electrochem. Soc. 118 (1971), 3, 428 – 433.

20) Y. Okinaka, C. M. Whitehurst, "Charge acceptance of the Cd/Cd(OH)$_2$ electrode at low temperatures", J. Electrochem. Soc. Vol. 117, No. 5.

21) G. Krämer, Electrochimica Acta 15 (1970) 1293.

22) VDE-Bestimmungen für Akkumulatoren und Batterieanlagen. VDE 0510 Ausgabe 1.77 (VDE Regulations for batteries and battery installations).

23) G. Neumann, DRP 975909 (1948).

24) H. Bode, K. Dehmelt, H. v. Döhren, Proc. Int. Symposium on Batteries 1958, Christchurch. Paper YY.

25) K. Dehmelt, H. v. Döhren, Proc. Annual Power Sources Conf. 13th. Ft. Monmouth 1959, pp. 85 – 89.

26) H. B. Lunn, J. Parker, Batteries 129 (1964).

27) Y. M. Pozin et al., Zh. Prikl. Khim., 46, 187 (1973).

28) E. J. Casey et al., "Nitrate shuttle", J. Electrochem. Soc. 112, 371 (1975).

29) IEC Publication 509 (1976) "Sealed nickel-cadmium button rechargeable single cells".

30) IEC Publication 285 – 1 (1969) "Sealed nickel-cadmium cylindrical rechargeable single cells, Part 1: General requirements and test methods".

31) AQAP-1, Nato-Forderungen an ein industrielles Qualitätssicherungssystem (1972) Stanag No. 4108 (1968). (NATO requirements for industrial quality control).

32) DIN 40729 Galvanische Sekundärelemente (Akkumulatoren), Begriffe

33) O. C. Wagner, D. D. Williams, "Investigations of charging methods for Ni-Cd batteries", USA ECOM 26th. Power Sources Symp. April/May 1974 p. 96 – 99. "Battery charging fashion" and M. Sulkes "Pulse charging", NASA Battery Workshop, Nov. 1976, USA ECOM.

34) DIN 820 Blatt 1, Normungsarbeit, Grundsätze (Standardization procedure, basic principles).

35) DIN 40764 Blatt 3, Nickel-Cadmium-Akkumulatoren, gasdichte Zellen, elektrische Prüfungen. (Nickel-cadmium batteries, sealed cells, electrical tests).

12. Formulae and Units

Symbol	Description	Units
a_j	Activities of reacting elements	$(-)$
A	Total surface area of the negative electrode	(mm², cm², dm²)
A_O	Maximum amplitude of a sine wave	(cm)
α	Angle of slope (TGI-charge)	(mV/°C)
b_{eff}	Effective acceleration of a noise (complex) vibration	(m/s²)
b_{max}	Maximum acceleration	(m/s²)
D	Diffusion constant for oxygen	(cm²/s)
DA	Peak-to-peak amplitude of a sine wave	(cm)
δ	Diffusion layer thickness	(cm)
f	Sine wave frequency	(Hz)
f_L	Charging factor	$(-)$
F	Faraday constant	(As/mol)
ΔG	Standard free enthalpy of reaction	$\left(\dfrac{\text{J/mol}}{\text{As/mol}}; \dfrac{\text{Ws/mol}}{\text{As/mol}}\right)$
η Ah	Ah-efficiency	$(-)$
η Wh	Wh-efficiency	$(-)$
i	Current density	(A/dm²)
I	Current	(mA, A)
K	Reaction velocity constant	(A/bar)
C	Capacity	(mAh, Ah)
λ	Failure rate	(%)
N	Load	(W)
v_j	Stoichiometric ratio	$(-)$
P	Partial pressure of oxygen	(mbar, bar)
P	Pressure at a given time of observation	(mbar, bar)
P_O	Initial pressure	(mbar, bar)
Q	Loss of heat	(J)
R	Gas constant	(J/mol K)
R_C, R_i	Concentration-, internal resistance	(Ω)
R_r, R_Ω	Reaction-, ohmic resistance	(Ω)
$R(t)$	Reliability	(%)
S	Solubility coefficient for oxygen	(mol/cm³ bar)
t	Time	(s, min, h, d)
t_E	Discharge time to end-of-discharge voltage	(s, min, h)
T	Absolute temperature	(K)
τ	Decay constant at standard pressure	(s, min, h)
V	Voltage	(V)
V_O	Cell equilibrium voltage	(V)
$V_{o,s}$	Cell equilibrium voltage at unity activity of all the separate reacting substances	(V)

V	Volume of free gas in cell	(ml, l)
z	Number of exchangeable electrons in the equation	(—)
—	Ion/atomic radius	(pm, m)
—	Molarity	(mol/l)